TRACE ELEMENT GUIDELINES FOR

IRRIGATION WATERS IN THE

SAN JOAQUIN VALLEY

WATER RESOURCES CONTROL BOARD
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EXCUTIVE SUMMARY

The objectives of this study were to review available information related to water quality criteria for trace elements in irrigation water and to suggest water quality guidelines for the protection of crops and livestock under the specific conditions in the West Side of the San Joaquin Valley. The important specific conditions of this area are 1) alkaline soils that control the chemistry and plant availability of trace elements, 2) the soils must be leached to prevent the accumulation of salts in the root zone, 3) the waters that have potentially toxic concentrations of trace elements also have relatively high salt concentrations and demand relative large leaching fractions, and 4) drainage waters and underground waters that contain abnormally high concentrations of trace elements also have high concentrations of sulfate which affect soil chemistry and plant availability of some trace elements.

Selenium

Because of the relatively high concentration of selenium (Se) in the agricultural drainage waters of the West Side of the San Joaquin Valley (SJV) in California and the potential for reuse of these waters on salt tolerant crops, a reassessment of quality criteria for Se in irrigation waters for this area was needed. The specific conditions for this area that justified a reassessment were 1) the Se in the drainage waters of the West Side is largely in the selenate form (SeO_4) which is not adsorbed by soils and is thus readily leached from the root zone, 2) the waters containing high concentrations of Se have substantial concentrations of sulfate (SO_4) that dramatically reduce Se absorption by plants, and 3) the salinity of the waters that contain high Se concentrations demand leaching fractions that insure that Se is also leached from the root zone.

Recent research with alfalfa (Medicago sativa L.), the most sensitive irrigated crop on the West Side of the SJV because of the potential for Se toxicity in livestock, shows that this crop, when irrigated with sulfate waters, can tolerate up to an average soil solution Se concentration of 250 ug/L without exceeding the limit of 4 mg Se/kg of dry weight of forage. At leaching fractions of 0.2 to 0.3 which are required for successful productions of alfalfa irrigated with even moderately saline waters, the Se in the irrigated water can increase to 100 ug/L without exceeding the maximum tolerable average concentration in the root zone. Thus, the recommended maximum concentration of Se in sulfate irrigation waters of the West Side of the SJV is 100 ug/L. This limit will provide a margin of safety for all other irrigated crops.

Molybdenum

A guideline of 50 ug L^{-1} is suggested for this element for irrigation waters of the West Side. The previous guideline of 10 ug L^{-1}

is still considered to be appropriate for a general water quality criterion, but for the West Side with 1) soil alkalinity which favors mobility of Mo, 2) high leaching volume, 3) high concentrations of sulfate which reduced Mo absorption by plants, an increase to 50 ug L^{-1} seems justified. Molybdenum unlike Se (as SeO_4) is adsorbed by soils. Therefore, the approach to establishing guidelines must be modified to include adsorption and desorption processes which can be described by the relationships between amount of Mo adsorbed per unit weight of soil and the concentration of Mo in the soil solution. The adsorption-desorption processes buffer the soil system against rapid changes in Mo concentrations. Thus, to establish a guideline one must know the quantities of Mo added, the concentration in the water and rates of removal in drainage waters and in harvested plants extrapolated over a period of time in years or decades.

To maintain a permanent irrigated agriculture the input of Mo in irrigation water must be balanced by outputs at a level of available Mo in the soil that is below the threshold for adverse effects on crops and animals. The outputs are removal in harvested crops, leaching beyond the root zone and conversion in the soil to residual forms. The information that is available suggests that for the protection of bovine animals that consume alfalfa hay the maximum Mo concentration should not exceed 50 ug/L for waters used on the West Side of the SJV. The Mo input for this concentration assuming an annual water application of 10.000 m^3/ha will be 0.5 kg/ha. In making this recommendation we are assuming that the sum of removals in crops, leaching losses and conversions in the soil to residual or unavailable forms will in the long term equal the inputs. Based on reported information, we feel that this recommended maximum concentration will provide protection for a number of decades if not indefinitely.

Arsenic, Chromium and Fluoride

A comprehensive and updated review produced no evidence that the water quality criteria for these elements should be changed. Consequently the existing guidelines of 100 ug L^{-1} for As and Cr and 1000 ug L^{-1} for F are recommended for the West Side.

Aluminum, Lithium, Nickel, Lead, and Vanadium

A review of the pertinent literature dealing with these elements suggests no changes in the guidelines recommended by the National Academy of Sciences (1973). Consequently we recommend that concentrations in irrigation waters for the SJV not exceed 5, 2.5, 0.2, 5 and 0.1 mg/L, respectively, for Al, Li, Ni, Pb, and V. For citrus the recommended maximum Li concentration is 0.075 mg/L. However, concentrations of these elements in irrigation waters of the SJV (Deverel et al., 1984) suggest no potential problems. Concentrations of elements such as Pb that accumulate in soils should be kept as low as possible.

INTRODUCTION

News of death and deformities among nesting waterfowl at Kesterson National Wildlife Refuge near Gustine in California's San Joaquin Valley (SJV) began to surface in 1983. By then, naturally occurring Se in soils of the San Luis Drain Service area had been identified as the most likely agent responsible. The Se was thought to be leaching out of the soils as an unanticipated consequence of irrigation by growers in the area.

The ongoing evaluation of water quality impacts resulting from irrigation return flows in the SJV is expected to result in additional reuse of drainage waters. This situation, although site specific, is typical of the west side of the SJV, where favorable soil factors and conditions (i.e., sulphate, selenate and leaching) reduce the concentration of available Se in the soil or in irrigation water. Until recently, the suitability of drainage water for reuse has been judged by concentrations of salinity, sodium adsorption ratio (SAR), boron, soil permeability and salt tolerance of crops. However, minor elements such as selenium must be taken into consideration to protect the soil resource, prevent crop damage, and protect animal and human health when the crops are consumed by livestock, as well as by humans.

Guidelines have been developed to evaluate the levels of trace elements in irrigation water (National Academy of Sciences, 1973). These guidelines, however, were developed for broad application and need to be reviewed for site specific use. Because of the unique soil, water and crop systems of the SJV, especially the western portion, a review of these guidelines was needed.

Over the past 15 years, a large amount of research has been done on trace elements in wastewaters and sewage sludge and their interactions with soil and crops. A review of recent research findings, however, was needed to develop data on characteristics of the water being considered for reuse in the west side of the SJV.

OBJECTIVE

National guidelines for trace elements in irrigation water were developed by the Committee on Water Quality Criteria of the Environmental Studies Board of the National Academy of Sciences (NAS)-National Academy of Engineering, and published in 1973. They were based on limited information and were rather conservative because they were intended to cover large ranges in conditions of crops, soils, climates and levels of management.

The West Side of the San Joaquin Valley (SJV) represents an area where selenium (Se), molybdenum (Mo) and perhaps other trace elements such as As are of acute concern. The SJV is an area having an arid climate and mainly fine textured alkaline soils devoted to the production of a number of specific crops. Also, considerable new information is available on some if not all trace elements of concern in irrigation water. Thus, there was an opportunity and a need to update the information available on trace elements and to apply it to the development of water quality guidelines specifically for the West Side of the SJV to protect crop and livestock from detrimental effects of these elements.

THE STUDY AREA

The San Joaquin Valley (SJV), the southern half of the great Central Valley of California, extends approximately 250 miles north from the Tehachapi Mountains to the San Joaquin River-Sacramento River Delta. The SJV averages 50 miles in width to encompass 8.5 million acres of valley floor, flanked by the lofty Sierra Nevada Mountains to the east and low-lying Coast Range to the west. The geologic history of the coast ranges (Norris and Webb, 1976; Taliaferro, 1940) is of particular importance in determining the soil characteristics responsible for many of the drainage, salinity, and toxicity problems in western SJV agriculture.

The SJV has a warm climate, relatively little frost, low rainfall and a large annual water deficit. A large part of the valley, particularly the southern third and the westside, receives 250 mm (10") or less precipitation while the loss of water either through evaporation from open water surfaces or from irrigated soil is as much as 1000 mm (39") per year. Thus, if precipitation is the only water source, there is a deficit of nearly 760 mm (30"). The result is that natural vegetation in the valley is grassland composed of species that are annuals — green only during the rainy season, and yellow-brown and dry the remainder of the year.

The SJV has a great variety of soils. The topography of the valley bottom — basins, alluvial fans, flood plains, stream ridges or terraces — results in various soil types with agricultural practices and crops adapted to them.

Soils on the west side of the valley are developed on alluvial fans and flood plains. They are light colored, low in organic matter, fine textured and nearly all are alkaline or calcareous (Storie and Weir, 1951). Typical soil series are the Panoche, Panhill, Orestimba, and Vernalis. Among the crops that grow in this area are cotton, sugar beet, wheat, barley, alfalfa, grasses, grapes, potatoes, tomatoes, peppers, onions, garlic, melons, and others.

The main problem relates to discharges of agricultural drainage from irrigated land in the West Side of the SJV to Kesterson Reservoir, the Grassland area of Merced County and the SJ River. Historically, the introduction of irrigated agriculture to arid areas has presented drainage problems. The unique geology, climate and hydrology of the west side of the SJV make the drainage problem particularly complex. Evapotranspiration rates are high, drainage is poor, and the drainage water contains not only salts but a complex mixture of other materials which occur naturally in the soil. If just enough water is used to replace what the crops use in evapotranspiration, over time, salts and other materials dissolved in the water will accumulate in the root zone and eventually render the area unsuitable for agriculture. If extra water is applied to flush soluble salts into the soil below the roots of

the plants, over time, the water will be stopped by the underlying clay layer and will rise toward the surface, drowning the roots and carrying the salts and other materials back into the root zone.

Minor elements, however, such as selenium, that are found in the soil parent material and consequently in the drainage water of the west side of the SJV are the subject of this report.

The environmental biological impact of selenium is probably more closely associated with geological and climatic factors than any other element. Areas producing forages with selenium concentrations sufficiently high to produce chronic toxicity to livestock tend to occur as localized "hot spots" in the west North Central region of the United States and scattered through the inland west. Soils associated with selenium toxicity in livestock are exclusively restricted to areas where they are formed from sedimentary parent material (especially shale) in association with low rainfall. All of these soils are neutral to alkaline in reaction, but as Kubota and Allaway (1972) emphasize, only a small fraction of the alkaline soils in their study regions produce plants with high-selenium contents. On the other hand, soil reaction is also important.

Geologically, granitic and basaltic rocks contain the lowest levels of selenium (mean 0.05 mg Se/kg), and higher levels are found in sedimentary rocks (mean in shale, 0.5 mg Se/kg) (Bowen, 1979). But shale deposits (even within the same formation) are not uniformly high in selenium, so that some fans on the west side of the San Joaquin Valley undoubtedly have lower selenium contents than are apparently presently found in at least a part of the Panoche Fan.

Another important factor is that the flow from the west-side creeks tended to spread out in the lower reaches of the fans and disappear into the soil. The flow seldom reached the San Joaquin River, and thus the salts from the shales in the mountains accumulated by evapoconcentration in the lower part of the fans. It is this part of the fan which is now receiving irrigation water. The perforated plastic pipe drains installed in these fields are now removing drainage water which has picked up the very soluble sulfates and chlorides, thus accounting for the very high TDS values (Burau, 1984).

Without elaborating on the details, the selenium in these surface materials (shale in the mountains, sediments in the fans) has tended to follow the sulfur. The predominantly sulfate form of sulfur in the shales is an indication that the selenium in the shales has also been oxidized to the more mobile selenite and selenate forms. It is expected that these will be the dominant forms (Burau, 1984).

The geological formations underlying the San Joaquin Valley are of sedimentary and volcanic origin. The west side of the valley is underlain primarily by marine sediments which contain high concentrations of selenium. The agricultural drainage water from highly seleniferous

soils of the west side of the valley is likely to contain relatively high salinity, boron, molybdenum, arsenic, and probably some other heavy metals.

Soil reclamation requires irrigation and subsurface drainage. The consequence with these actions is that the drainage waters contain high concentrations of selenium and other trace elements from the soil. In order to predict how much selenium or others may be leached, it is necessary to determine not only the concentrations of trace elements in the soil, but also their chemical forms. Generally, in the sedimentary material found on the west side of the valley, selenium and sulfides co-occur. The sulfides rapidly oxidize to sulfates which are leached out, and are eventually replaced in the mineral matrix by selenium. Irrigation and subsurface drainage may also increase the rate of oxidation of selenium, and consequently increase its leachability.

THE PRESENT PROBLEM

Agricultural drainage water from the western San Joaquin Valley represents a serious source of salts, selenium and other trace elements. Soils in certain parts of the western San Joaquin Valley contain high levels of salts and trace elements, most notably Se. As more lands have come under irrigation, water that percolated through the soil began to accumulate above a subsurface clay layer found to extend under virtually the entire region. The severity of this drainage problem increased with time and eventually required the installation of subsurface tile drains in a large number of acres of irrigated fields to remove the accumulated water and salt from the crop root zone. At present, subsurface drains have been installed in 125,000 acres of agricultural lands in the western San Joaquin Valley, leaving another 156,000 acres with serious drainage problems that may also require subsurface drains (Personal Communication).

The shallow groundwater in the western San Joaquin Valley, which is collected in subsurface drains for discharge, was analyzed for Se and other trace elements (Presser and Barnes, 1984). The results identified three toxic elements of major concern: chromium, mercury, and selenium. All three were found in concentrations approaching the criteria levels established by the EPA to protect freshwater aquatic life. Selenium was detected in 76 percent of the samples, and was found in higher average concentrations in the central (10 ug/L) (parts per billion: ppb) and western (11 ug/L) (ppb) portions of the area than in the eastern lands adjacent to the San Joaquin River, where the average selenium concentration was less than 1 ug/l (ppb). The highest selenium concentrations found in the study, up to 3,800 mg/l, were located in a semicircular area extending approximately 15 miles north, west, and south of Mendota (Deveral et al., 1984).

This high-selenium area corresponds to the alluvial Panoche Fan, which contains selenium deposited by the Panoche Creek from selenium-bearing rock in the Coast Range, and the Panoche Fan covers 220,000 acres of primarily irrigated farmland (USBR, 1984).

The problem is what to do with the drainage water so that it does not create an environmental hazard. One solution involves reuse of the water for irrigating salt tolerant crops to concentrate the salts and toxic elements into smaller volumes of water thus reducing the disposal problem. The safe use of drainage waters, however, creates the possibility of excess selenium, molybdenum and other trace elements in forage or grain fed to animals. Thus, some water quality guidelines for trace elements in irrigating soils of the west side of the SJV are needed.

APPROACHES TO THE ESTABLISHMENT OF GUIDELINES

A meaningful guideline for the concentration of any given constituent in irrigation water should consider such factors as 1) crop sensitivities, 2) soil properties, 3) the reactions of the constituent with soil solids, 4) climatic factors, 5) management level, 6) irrigation system, 7) interactions with other constituents in the water and 8) economic conditions that determine how much reduction in yield or quality can be tolerated. Crop sensitivities include not only yield relationships but also concentrations of the constituents in plant products that are toxic to livestock and in foods for man. In other words the adverse effects of the accumulation of a constituent in the root zone consist of reduction in yield or quality of harvested products, toxicity to animals that consume forages or grains and toxicity to humans through consumption of plant and animal products.

To avoid the accumulation of toxic amounts of trace element in the root zone of irrigated lands the inputs in irrigation waters must be limited, in the long term, to losses from the soil and conversion to unavailable forms in the soil. Losses include removal in harvested products, leaching in drainage waters and erosion by water and wind. Losses by volatilization of gaseous compounds for most trace elements is unlikely but should be considered for some elements under certain conditions. The importance of the conversion to unavailable forms in the root zone can range from insignificant for Se in the SeO_4 form to the dominant factor with elements such as Pb and Cu. On the other hand, Se in the SeO_4 form is completely mobile, moves with the soil water and is easily leached, whereas Cu and Pb move so slowly that leaching losses can be completely ignored in most soils. For most trace elements the removal in harvested products is small but over decades it must be considered as one of the important outputs that balance inputs.

The approach or rationale for the selection of recommended maximum concentration of trace elements depends to a great extent on the mobility or the ease with which the element can be leached. If the element is highly leachable, such as Se in the SeO_4 form, the approach can be the same as for total salinity or the chloride anion which is not adsorbed by soil solids. In this case the toxicity level (for plants, animals or man) can be established in terms of the mean concentration in the root zone for each crop to be grown. The recommended maximum concentration can then be determined for each crop and for various predicted leaching fractions that depend on the soil and on irrigation practices. With such an element the accumulations during the growth of highly tolerant crop can be removed by leaching before a highly sensitive plant is grown. Thus, recommended maximum concentrations in irrigation waters can be established for various crops, soils and irrigation systems giving considerable freedom to adjust the guidelines to local conditions.

If the element in question is not mobile and leaching losses are so small as to be insignificant a different approach must be taken. The inputs that are not balanced by removal in harvested products and conversion to unavailable forms accumulate in soluble or labile forms. The relationships among these forms can be expressed in the general equation

$$\text{Soluble} \;\rightleftharpoons\; \text{Labile} \;\rightleftharpoons\; \text{Residual}$$

in which the soluble element is adsorbed or desorbed into the labile form as the amount in solution increases or decreases and the labile or adsorbed element is transformed into the residual or unavailable form or released from the residual form as the labile form increases or decreases. The immediately available element is that in the soil solution. However, as the soluble element is removed by plant roots desorption from the labile pool replaces the soluble pool so that the toxicity level depends on both the amount in solution and the capacity of the labile pool to replenish the amount in solution.

The problem with elements that accumulate in soluble and labile forms in the soil is that once toxic levels are attained elimination or reduction of these levels is an extremely slow process involving removal in harvested crops and the slow conversion to residual forms. When toxic levels occur for a given crop decades may be required before this crop can be grown again even if inputs of the element cease and the farm manager becomes restricted to the production of more tolerant crops. The safe approach in these situations is to limit inputs to protect the most sensitive crop, to maintain the freedom of the manager and to avoid toxicities to plants, animals and man for an indefinite period of time.

Selenium in the SeO_4 form is an example of the mobile elements for which the soluble anion approach can be used to establish criteria or guidelines for each crop for various management and soil conditions. Arsenic is an example of the elements that accumulate in solule and labile forms for which guidelines must be established or selected to protect the most sensitive crops.

SELENIUM

Introduction

Despite the recent flurry of attention it has received, selenium is hardly a new discovery; its beneficial uses and applications, and its potentially toxic effects have been known or suspected for many years. As early as 1842 its toxicity was documented (Japha, 1842, as cited by Moxon and Rhian, 1943). Selenium's connection to western rangeland food chains through soil, water, and plants has been known for decades by stockmen and scientists familiar with alkali disease, or the "blind staggers", as it is sometimes called (Moxon and Rhian, 1943). Centuries earlier, Marco Polo noted symptoms of what is now recognized as selenium poisoning in his horses while he was traveling on China's Silk Road. No doubt the Chinese residents of Xinjiang Province were already familiar with the disease, if not its cause, before Marco described it to the European community. On the other hand, a more recently described disease is Keshan disease, which is attributed in humans to selenium deficiency. Keshan disease has been reported from China (Burau, 1985). Much, however, remains to be learned about selenium's role in animal, human, and plant metabolism, and about its behavior in bio-geochemical cycles.

Selenium is not an agrochemical applied to crops or soil. It is associated with agriculture in the western and southern SJV because irrigation has mobilized the selenium which naturally occurs in some soils. Drainage water from selenium-laden soil contains high concentrations that have contributed to the documented toxicity to wildlife at Kesterson Reservoir.

Dissolved Se concentrations in drainage water vary widely. Because knowledge of the areal distribution of Se is important in developing an efficient water management plan and guideline for western San Joaquin, intensive investigations are being conducted to develop this information. Deverel et al. (1984) reported that selenium concentrations in shallow groundwater in the western SJV are extremely variable and can range from undetectable to several thousand ug/L. The Deverel data indicate that Se concentrations are generally low in the basin trough zone and in the northern part of the alluvial fan zone. On the other hand, drainage waters from either the alluvial fan or basin rim zone in the central and southern part may contain extremely high Se concentrations, the value of which is site-specific. The highest concentration measured in the San Joaquin River was 2 ug/L, a level well below the public health standard of 10 ug/L for drinking water.

Physical and Chemical Properties

Selenium belongs to the oxygen-sulfur family of elements and is chemically similar to sulfur and tellurium. Selenium combines directly with oxygen, hydrogen, nitrogen, the halides, and most of the common metals. Like sulfur, elemental selenium occurs in several crystal and amorphous forms or allotropes. Amorphous or non-crystalline selenium occurs as a red powder, a black mass, or as a colloid. Monoclinic crystalline selenium is a deep red; the hexagonal variety, the most common, is metallic gray to black. All of these forms are insoluble in water.

Selenium's current notoriety scarcely reflects its abundance: it is one of the less common elements, falling between mercury and gold in abundance, and averages about 0.05 parts per million (ppm) in the earth's crust. Elemental or native selenium (Se^0) is rare, although it does occur in some sediments and is occasionally mixed with native sulfur. More common than the elemental form are the various chemical combinations of selenium with other cations, mostly metals or metalloids. In these combinations selenium behaves chemically as a nonmetal. There are three common oxidation states of selenium: selenide (Se^{-2}), selenite (Se^{+4}), and selenate (Se^{+6}).

Depending on its valence state selenium can behave either as a reducing agent or as an oxidizer. In its higher valence states selenium is a strong acid-former. It reacts with hydrogen at temperatures below 250^oC to form a very toxic gas, hydrogen selenide (H_2Se), which decomposes quickly in the presence of oxygen. This gas also may be prepared by allowing dilute acids to react with metallic selenides such as sodium selenide (NaSe), iron selenide (FeSe), or aluminum selenide (Al_2Se_3) (Stone, 1968).

Solubility of selenium compounds varies considerably, from very high (over 40% by weight) for sodium selenate, to very low (0.16 to 0.33 grams per liter) for silver selenate. Heavy metal selenides are insoluble, as is elemental selenium (National Academy of Sciences, 1976). The elemental form is generally rather nonreactive; it also is not readily reduced or oxidized.

Selenium in the Diet

Selenium's role in human and animal diets is extremely complex and poorly understood (Figures 1 and 2). As is the case with most trace elements in the diet, selenium's effects differ significantly according to the quantities consumed. A minor amount (just how much is unknown) of selenium is necessary in the diet of humans and animals. Its importance in plant metabolism is still incompletely understood.

In California, Se deficiency in livestock is common. Worldwide, problems and losses of livestock due to Se deficiency historically have been greater than those due to selenium excess (Lakin, 1973). A

considerable world body of literature exists which describes symptoms of dietary deficiency and excess of Se in horses, pigs, sheep, cattle, and chickens. The symptoms of Se poisoning have been known for some time: softening and loss of hooves, loss of hair, uncontrolled appetite (which includes eating inappropriate items), staggering, listlessness, immobility, and finally, painful death (Moxon and Rhian, 1943). Deficiency is likely if Se concentration in food is less than 50 parts per billion (ppb). Toxicity probably begins between 3,000 to 5,000 ppb, and Se balance likely is achieved between 100 to 1,000 ppb.

Selenium is an essential element for the growth and proper function of a variety of aquatic and terrestrial animals, but can be toxic at low concentrations in nutrient solutions. The minimum selenium requirements of animals vary with the form of the element ingested and the nature of the rest of the diet. A dietary selenium intake of 0.1 ug/g is thought to provide a satisfactory margin of safety to be encountered by grazing sheep and cattle (Allaway and Hodgson, 1964), while concentrations exceeding 4-5 mg Se kg^{-1} in animal feed is considered potentially toxic for grazing livestock (Underwood, 1977).

Little is known about the effect of Se on wild animals, fish and fowl. A fairly recent summary of the present state of knowledge of the effect of Se is found in the ambient water quality report for Se by the U.S. Environmental Protection Agency (1980, 1987; Marshall, 1985).

Effects of Se toxicity on humans are less well known than the effects on animals. Selenium toxicity in humans is relatively rare, in part because of modern food distribution techniques, which bring to the diet items from many different regions. A study in China (Chen et al., 1980; Burau, 1985) recorded symptoms of Se toxicity in a population of peasants who, forced by drought to rely more heavily than usual on vegetables grown locally in Se-rich soils, began to show such symptoms of Se poisoning as loss of nails and hair and skin lesions. In the Chinese study no toxic symptoms were noted in individuals consuming less than 750 micrograms per day of selenium, but one or more symptoms of chronic Se toxicity appeared in persons consuming 5,000 micrograms or more per day.

In the United States, the recommended adult dietary allowance of Se is 50-200 micrograms per day (Brooks, 1984). For drinking water, the standard used by the National Academy of Sciences and the U.S. Environmental Protection Agency (1980) is 10 micrograms of Se per liter, but some consideration is being given to raising it to possibly 50 ug/L. Average U.S. consumption of Se is approximately 170 microgram per day from all sources (Burau, 1985). A diet which contains approximately 1,000 to 5,000 micrograms per day could produce chronic selenium toxicity (selenosis), with loss of hair and fingernails, skin lesions, and digestive disorders. More advanced symptoms of selenosis are generalized numbness, paralysis, convulsions, and death. The effects can be alleviated by adopting a low-selenium diet (Hartshorn, 1985).
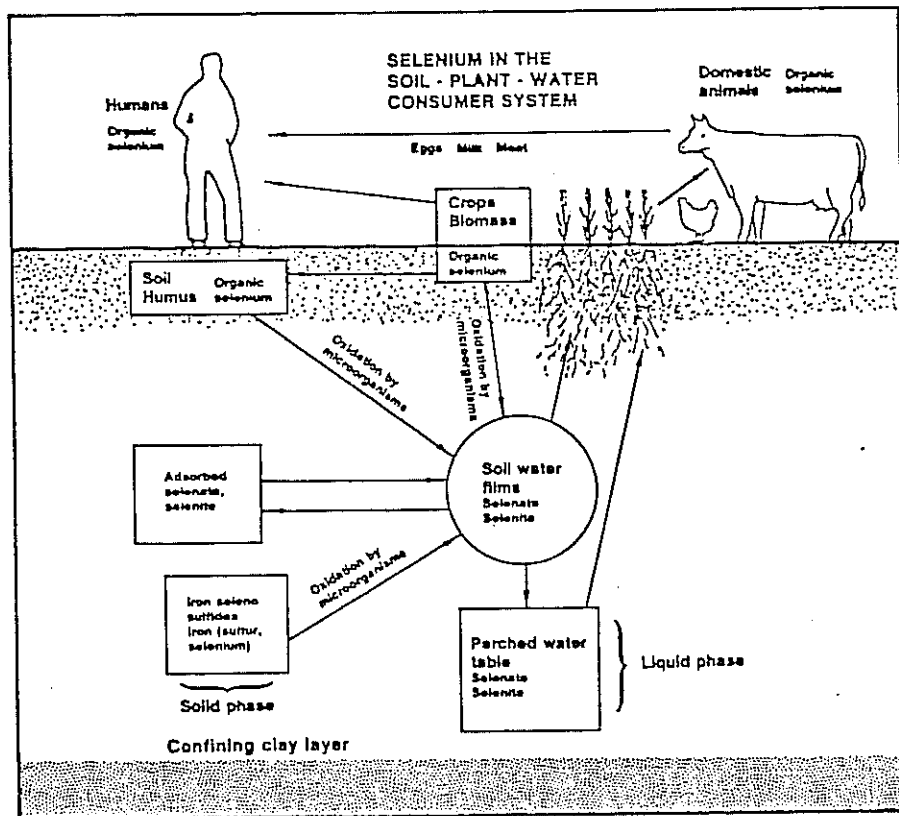
Figure 1. Plant roots take up selenate (Se⁺⁶) or selenite (Se⁺⁴) forms of selenium from the soil water. The selenium concentration in solution depends on the solubility of the forms of selenium present and the biological transformation of organic forms. *By Burau (1985, p. 18).*
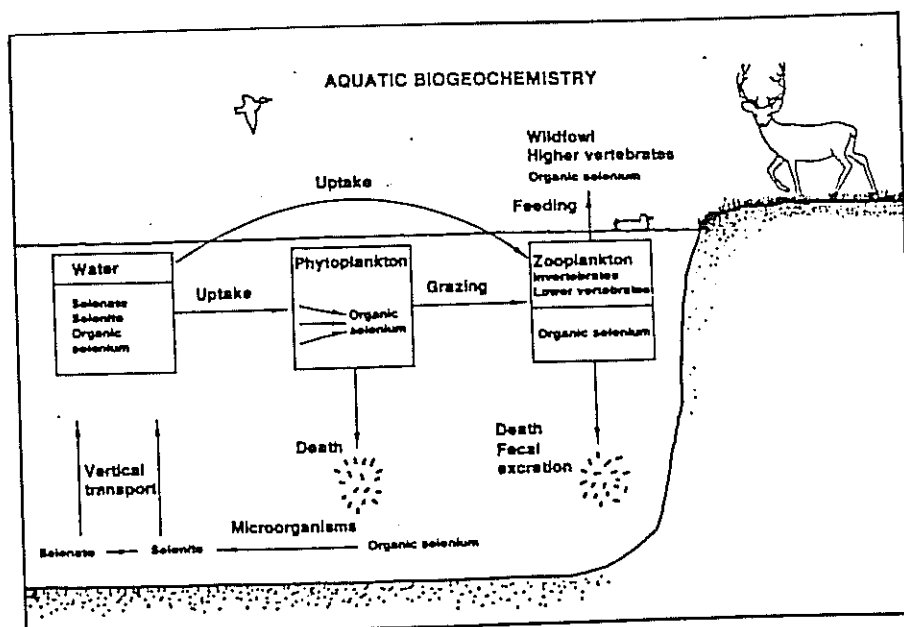
Figure 2. Aquatic organisms such as marsh plants, plankton, and insects take in inorganic selenium and transform it into organic forms. The organic forms of selenium are then more easily taken up by higher life forms such as wildfowl and mammals. *By Burau (1985, p. 18).*

Based on studies of animals the U.S. drinking water standard was set on the basis of concern over selenium's possible role as a carcinogen. However, the evidence is contradictory and inconclusive (U.S. Environmental Protection Agency, 1980); there is some indication that non-toxic amounts of Se salts may inhibit tumor formation.

Experiments with barley, Drosophila flies, rabbit kidney tissue cultures, and human white blood cell cultures suggest that at higher dietary levels, Se may act as a mutagen that causes genetic changes. In addition, a number of studies dating back to the 1950s have implicated Se as a teratogen that causes defects in the developing embryo. Deformities induced by Se have been recorded in chickens, turkeys, rats, cattle, and other domestic animals (U.S. Environmental Protection Agency, 1980; National Academy of Sciences, 1976). Selenium may be a teratogen in humans (U.S. National Academy of Sciences, 1976).

Selenium in Soils

Selenium is widely distributed in soils. Usually its concentration is low, approximately 200 to 400 ppb in an average soil worldwide (Wiggett and Alfors, 1986). Some soils are selenium-deficient, cattle fed on these rangelands must be given selenium supplements in their diets. Selenium-poor soils may contain as little as 100 ppb selenium. In California such soils occur on the eastern side of the San Joaquin Valley, where they are derived from the weathering of selenium-poor Sierra Nevada granitic and metamorphic rocks.

Selenium may be abundant in soils derived from the weathering of sedimentary rocks, particularly marine pyritic shales. Such soils are widely distributed in western North America particularly in areas of dry climate where the parent rock is Cretaceous or Tertiary marine shale. For example, seleniferous soils in Nebraska, South Dakota, Wyoming, Kansas, and Colorado are all developed on the Upper Cretaceous Pierre Shale or on the Upper Cretaceous Niobrara Formation (Moxon and Rhian, 1943). In these areas, the soils, or occasionally the incompletely weathered shales, may support vegetation which has concentrated enough selenium to be toxic to grazing animals. Selenium contents as high as 6,000 to 28,000 ppb have been reported in soils developed on the Pierre Shale (Burau, 1985).

Glacial drift in North Dakota and Canada and glacial lake sediments have been suggested as selenium source rocks for soils which support seleniferous plants. There have also been reports of selenium in units older than Cretaceous, including some soils developed on Permian-Triassic rocks in Wyoming and Idaho (Moxon and Rhian, 1943; Ganje, 1966).

In California, selenium-rich soils are found at lower elevations on the west side of the San Joaquin Valley. Selenium-rich soils are especially common in the alluvial fans of the Panoche area (Figures 3 and 4). Although little is actually known about the distribution of
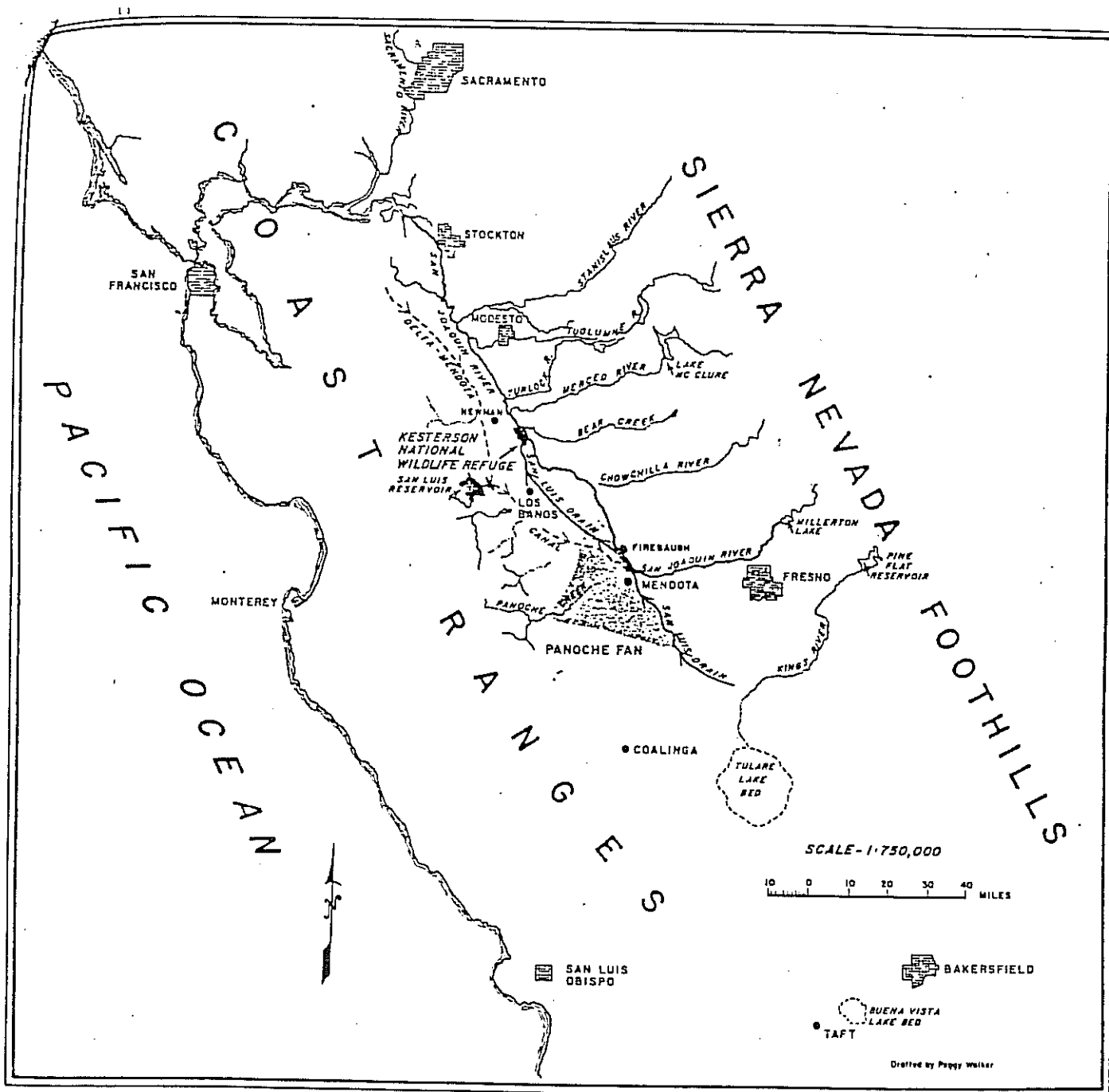
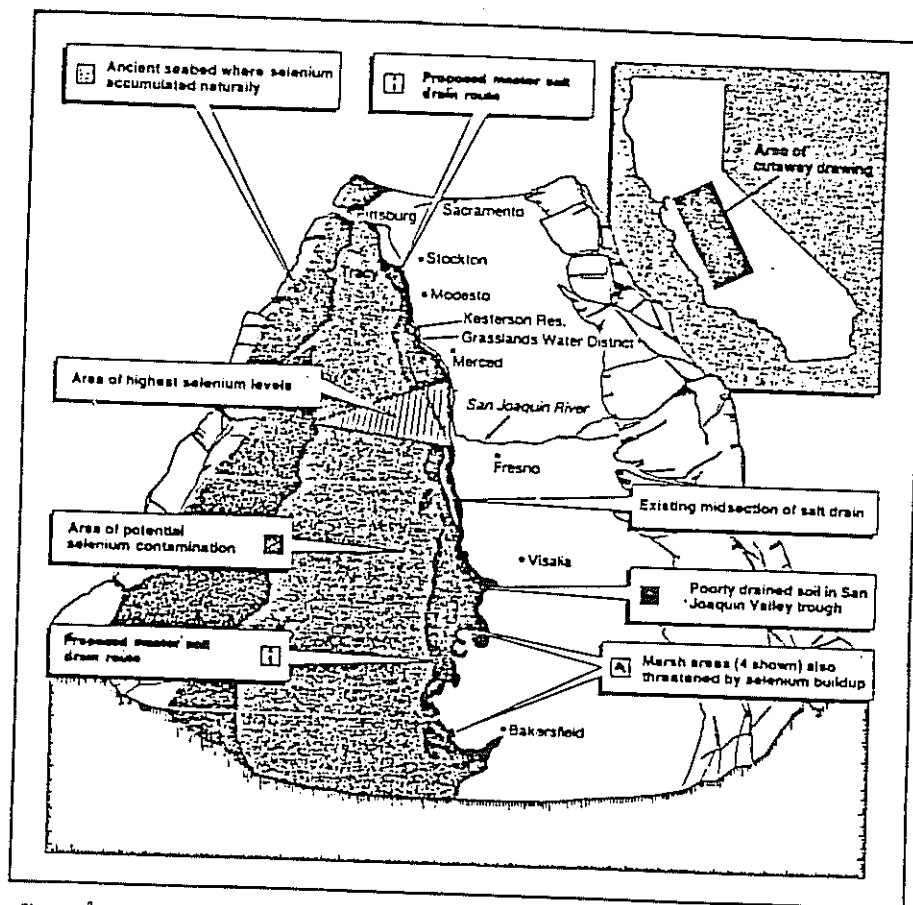Figure 3 The San Joaquin Valley of California.

Figure 4 Areas of selenium buildup in the San Joaquin Valley. *Figure by Jim Chaffee, courtesy of The Sacramento Bee.* Cited by Wiggett and Alfors, 1986.

selenium in the Coast Ranges, selenium in the Panoche Fan area may have come from Cretaceous and Tertiary pyritic shale units such as the Moreno Formation in the Diablo Range (Lakin and Byers, 1941; U.S. Bureau of Reclamation, 1984; Sylvester, 1985).

While a number of conditions may lead to the production of seleniferous soils, not all selenium-rich soils are associated with diseases of selenium toxicity. In North America, seleniferous soils producing toxic vegetation belong to the pedocal category, and are confined to regions with a mean annual rainfall of less than twenty inches (Ganje, 1966). In contrast, seleniferous soils, such as those in Hawaii, do not produce toxic vegetation.

The key to the problem of soil toxicity is the chemical state of the selenium which is present. Selenium may occur in soils as elemental selenium, as selenide, selenite, selenate, or as organic selenium. Of these, common selenium salts are ferric selenite $[Fe_2(OH) + SeO_3]$ and calcium selenate $(CaSeO_4)$; elemental selenium is quite rare in soils. Where soils have supported selenium-accumulating vegetation, up to 40 percent of the soil's selenium content may occur in the surficial humic layers, contributed as organic selenium by decayed vegetation. However, studies have shown that the principal source of selenium for plants is in the lower portions of the soil profile, where, in alkaline soils of dry climates, the water-soluble selenates accumulate. In acidic moist-climate soils, selenium accumulates as low-solubility selenites, which are unavailable to plants (Moxon and Rhian, 1943).

The water soluble fraction of soil Se is considered to be the fraction available to plants. Van Dorst and Peterson (1982) reported the close positive correlation between the Se content of plants and the selenate ion concentration in the soil solution. However, other Se fractions may also be soluble in soils, and thus Elsokkary (1980) concluded that, on the average about 45% of the total soil Se could be available to plants and that plant available fractions could be extracted with K_2SO_4 or NH_4OH solution. The presence of soluble SO_4^{2-} in the soil, or in the irrigation water may be a major soil factor in determining the accumulation of Se by plants, and consequently the rate of Se uptake (Pratley and McFarlane, 1974; Spencer, 1982; and Mikkelsen et al., 1987).

The solubility of Se in most soils is rather low; therefore, many agricultural areas produce crop plants and forage with low Se contents. However, in natural Se-enriched soils, in poorly drained or calcareous soils, in soils of acidic zones, and also in soils heavily amended with sewage sludges or fly ashes, Se may be accumulated by plants in concentrations high enough to be toxic to grazing livestock.

Ground and Surface Waters

Commonly, fresh water is slightly acidic and the associated selenium usually occurs as selenite (Se^{+4}) (Brooks, 1984). Under a combination of acidic and reducing conditions, selenite is reduced to

relatively insoluble elemental selenium (Deveral et al., 1984), which accumulates in the sedimentary substrate (National Academy of Sciences, 1976). However, in alkaline water, such as found in the west side of the San Joaquin Valley, selenate (Se^{+6}) is the most common form. Selenate is the most common form in waters and soils and is the form most available to plants. Algae incorporate the inorganic selenium into amino acids and proteins, thus permitting the element to enter the animal food chain (Brooks, 1984).

Selenium levels in fresh and marine water worldwide average approximately 0.2 ppb and 0.1 ppb respectively (Hem, 1985). Levels may be three or more orders of magnitude greater in seepage water in areas of seleniferous soils. In California, selenium content of surface water in the east side of the SJV is low (less than 1 ppb) (Regional Board files, 1981), but in the west side of the valley in the area of Kesterson Reservoir, San Luis Drain and the Panoche fan some selenium levels have been found to be as high as 4,000 ppb in drainage waters (Figure 4) (Burau, 1985). Selenium levels of algal mats and salt crusts from ponds on the San Luis Drain contain up to 20,000 ppb selenium (Deverel et al., 1984; Presser and Barnes, 1984; 1985).

The Department of Water Resources' 1984 SJV drainage monitoring activities consisted of collecting water samples from 16 subsurface drains and 2 surface drains in the central and southern areas (Bakersfield, Kern and Kings Counties). The department analyzed water samples for pertinent nutrients, minerals, pesticides, trace elements including Se and other constituents (SJV Drainage Monitoring Program 1984, District Report - 1986). Se concentrations varied from 0 to 0.420 mg/L in the central area and from 0 to 0.02 mg/L in the southern area.

The processes by which selenium has become concentrated in the irrigation drainage water and other water of the Kesterson area are not well understood (Deverel et al., 1984). One hypothesis suggests that the selenium, originally derived by weathering and oxidation of sedimentary selenosulfides ($SeSO_3^{-2}$) in marine shales of the Coast Range, is released as selenite ($Se+4$) and selenate (Se^{+6}) salts, while the sulfides go into solution as sulfates (SO_4^{-2}). These materials are then deposited in the alluvial fans on the valley floor, where they are concentrated by evaporation. Later, the oxidized selenium, which probably is highly soluble under alkaline conditions in the area, is taken into solution by infiltrating irrigation water and/or shallow ground water (Presser and Barnes, 1984). Further evaporative concentration would occur during the irrigation process. Evaporation of shallow ground water would likely cause concentrations of selenium in some soils, particularly the saline soils in the rim area of the San Joaquin Valley basin.

Dissolved selenium carried by deeper ground water flow from the Coast Range to low lying discharge areas near the San Joaquin River has been suggested as a possible long-term process (Deverel et al.,

1984). Such a process may have occurred over geologic time, and may still be occurring in the western side of the San Joaquin Valley. The rate and amount of selenium transport would probably vary with long-term or even short-term variations in precipitation and recharge. In historical times, changing patterns of human use of surface and ground water had an impact on rates and patterns of selenium transport.

On the basis of the geochemistry of Se it seems to be possible to predict trends of Se behavior in a particular soil environment. Olson (1967) has presented a diagram illustrating the Se environmental cycle (Fig. 5). A generalized summary of Se species that may occur in soil is presented in Fig. 6.

Lakin and Davidson (1967), Allaway (1968 a&b), and Paasikallio (1981) have extensively reviewed Se behavior in soil and have emphasized its complex character. It can be generalized that:

1. In acid, gley soils, and soils with high organic matter content, selenides and Se-sulfides dominate — they are only slightly mobile and therefore hardly available to plants.

2. In well-drained mineral soils with pH close to neutral, selenites exist exclusively. Their alkaline metal compounds are soluble, but Fe selenites are not; moreover, selenites are rapidly and nearly completely fixed by Fe hydroxides and oxides and thus are very slightly available to plants.

3. In alkaline and well-oxidized soil selenates are likely to occur. They are easily soluble and are unlikely to be fixed by Fe oxides and may be highly mobile and readily taken up by plants.

However, several complex anions of Se as well as organic chelates greatly modify the behavior of Se in each particular soil. This has been nicely illustrated by various trends in Se distribution along soil profiles (Figure 7).

The solubility of Se in most soils is rather low; therefore, many agricultural areas produce crop plants and forage with a low Se content. However, in naturally Se-enriched soils, in poorly drained or calcareous soils, in soils of acidic zones, and also in soils heavily amended with sewage sludges or fly ashes, Se may be accumulated by plants in concentrations high enough to be toxic to grazing livestock.

The water soluble fraction of soil Se is considered to be the fraction that is available to plants. Van Dorst and Peterson (1982) reported that the behavior of Se in highly calcareous soil is of special concern because when soils are low in sesquioxides the Se becomes water soluble. Singh (1982) stated that the best effects in correcting Se toxicity to plants in such soils are obtained by the application of S, P, and even N onto the soils.
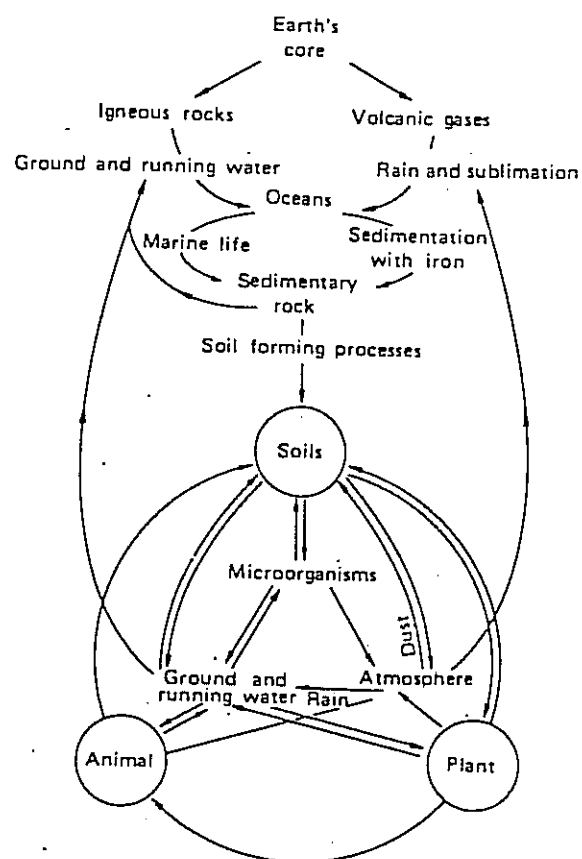
Fig. 5. Cycling of Se in nature [from Olson, O. E.: *Selenium in biomedicine,* Chap. 18, Westport, Conn.: Avi Publishing Co. (1967)].
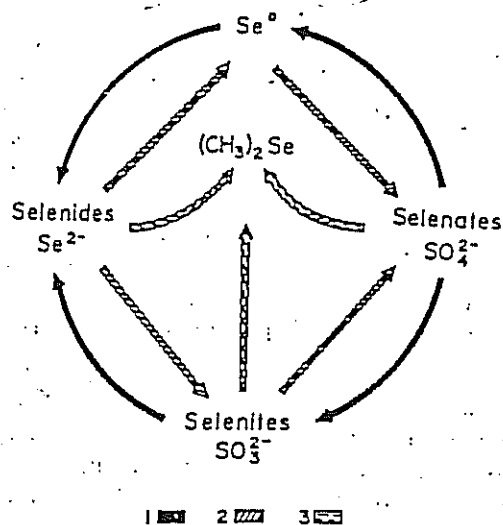

FIGURE 6 Ionic species and transformation of Se compounds in soils. (1) Reduction; (2) oxidation; (3) methylation.

Selenium in Plants

There is no evidence that plants require Se for growth and completion of their life cycles. Broyer et al. (1966), in carefully controlled greenhouse experiments, could not demonstrate a Se requirement for either alfalfa or subterranean clover.

Factors affecting the quantitative amounts of Se in plants include (a) concentration and plant availability of the element in the soil, (b) plant species, (c) climate and, (d) management practices such as fertilization, irrigation and drainage. These factors are discussed by Allaway et al. (1967), Bisbjerg and Gissel-Nielsen (1969), Cary and Allaway (1969), Johnson et al. (1967), Olson (1967), Rosenfeld and Beath (1964), Hamilton and Beath (1963 a and b, and 1964).

Although Se in plants has been investigated in many studies, its physiological role is still unknown. There are some opinions stating that Se may be involved in certain metabolic processes, especially in plants that are Se accumulators (Moxon and Olson, 1974), but the essentiality of Se for plant growth has not been conclusively established. The great interest in plant Se is due to the importance of this element in animal nutrition, particularly for domestic animals, since Se can act both as a micronutrient and a toxin. Furthermore, the margin of safety of Se concentrations in animal diets is rather narrow.

When present in soluble forms, Se is readily adsorbed by plants, though differences between plant species are commonly observed (Figure 8). The availability of Se is also controlled by several soil factors, among which pH is believed to be the most pronounced (Figure 9).

The uptake of Se by plants is also a temperature-dependent process; on a soil low in Se, plants absorb a much higher amount when the air temperature is >20°C than during cooler seasons with a temperature of <15°C (Lindberg and Lannek, 1970). Rainfall may also highly influence the Se concentration of herbage. As Reuter (1975) reported, low Se in plants frequently occurred in high rainfall areas.

There is a positive linear correlation between Se in plant tissues and Se content of soils, and Sippola (1979) stated that total soil Se gives a better measure of plant response than does its soluble fractions. In general, soil Se uptake by plants depends on climatic condition, water regime of soil, oxidation-redox potential, pH, and sesquioxide content of the soil.

The distribution of Se within plants differs, depending on several nutritional factors, but its concentration in growing points, in seeds, and also in roots was most often observed. Arvy et al. (1974), however, studied Se distribution between various tissues of corn and did not find any significant differences.
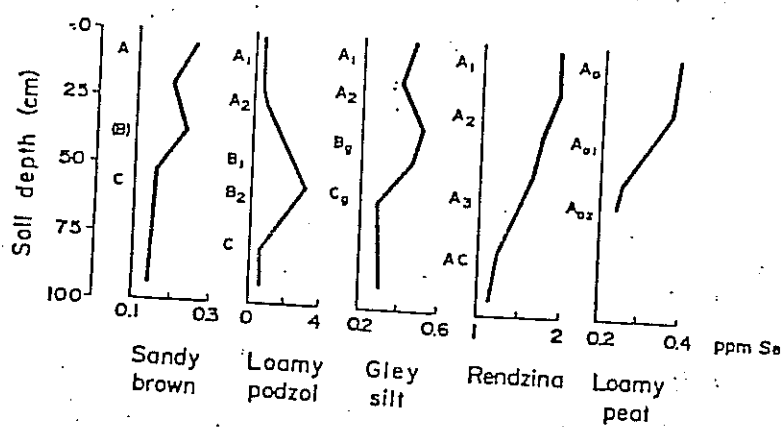
FIGURE 7 Distribution of Se in some profiles of soils in New Zealand. (Letters indicate genetic soil horizons.) Wells (1967)
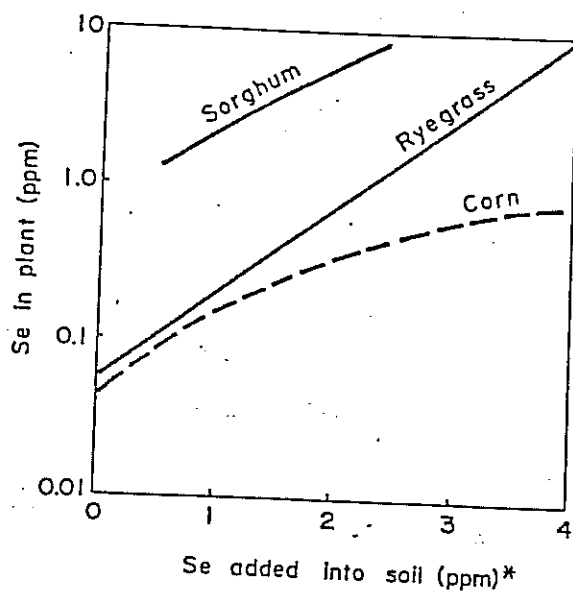

FIGURE 8 Influence of Se added as Na_2SeO_3 into the soil on Se content of plants. *Se level in soil in the experiment with sorghum is given in ten-times lower concentration (e.g., at the range of 0.05 to 0.25 ppm). Paasikallio (1981) and Singh (1982)
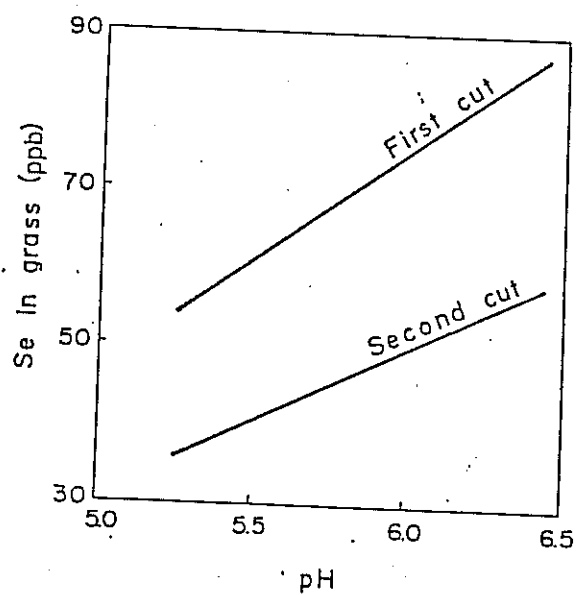
FIGURE 9. Se content of ryegrass as a function of the soil pH.

Singh (1982)

In plants, Se resembles S in its biochemical properties and is able to replace S in amino acids as well as in several biological processes. About eight Se-organic compounds have been identified in plants (Ganther, 1974). Amino acids, especially cysteine, are likely to bind Se, which may have several metabolic implications. Volatile Se compounds (i.e., dimethyl diselenide) isolated from plants, and from Se-accumulating species in particular, are known to be responsible for Se release from plants and also for the unpleasant odor of plants such as Astragalus (Evans et al., 1968).

The ability of a plant to accumulate and tolerate Se is apparently related to different Se metabolisms. Opinions vary, however, as to whether Se is incorporated in proteins or in nonprotein amino acids (Mengel and Kirkby, 1978).

Toxicity of Se to plants growing under natural conditions has not been reported, but symptoms of Se toxicity to crop plants have been described (Kabata-Pendias and Pendias, 1984). In culture solutions, toxic effects of Se on onion roots were observed by Fiskesjo (1979) at as low as 1 mg L^{-1} concentration. Also a decrease in yield of several crops was effected by the application of about 2 ppm Se onto the soil (Singh, 1982).

Increased Se levels in plants suppresses concentrations of N, P, and S as well as of several amino acids. Also the absorption by plants of heavy metals, mainly Mn, Zn, Cu, Fe, and Cd, is inhibited by increasing Se in the plant tissue. This relationship is dependent on the ratio between the elements, and thus some stimulating effects of high Se concentrations on uptake of heavy metals may also be expected.

The application of P, S, and N is known to help in detoxifying Se, which may be a result of depressing the Se uptake by roots or of establishing a beneficial ratio of Se to these elements, even when the Se content of plants is elevated. There is also a report that the addition of lime, S, B, and Mo to the soil under field conditions did not affect the Se concentration in plant tissues (Gupta and Winter, 1975). In practice, the application of S is an important remedial treatment on Se-toxic soils (Singh, 1982). However, as Johnson (1975) reported, S fertilizers are effective in preventing Se toxicity only to plants growing on low Se soils. As a resolution to this conflicting evidence, Mikkelsen et al. (1987) showed that in the presence of SO_4^{2-} salts, the plant-Se accumulation was reduced from 948 mg kg^{-1} to 6 mg kg^{-1} (dry wt. basis).

Ehlig et al. (1968) reported that differences among plant species in Se accumulation from soils low in Se were small, with the exception of seleniferous indicator plants such as Astragalus sp. or other legumes which concentrate Se to extremely high levels (up to about 1000 ppm dry wt. basis). The available systematic data concerning Se content of forage plants show that, for most countries, Se ranges in grasses from 2 to 174 ppb (dry wt. basis, mean 33), for clover and alfalfa ranges from

5 to 880 ppb (dry wt. basis, mean 99), and for other forage plants ranges from 4 to 870 ppb (dry wt. basis, mean 67).

Elements which can contaminate the food chain at plant tissue concentrations lower than those which cause phytotoxicity are not controlled by the "soil-plant barrier" and therefore may have to be controlled by limits on land applications as in the case with Se (Chaney, 1983). This element, however, has received little attention as a contaminant in sewage sludge (Logan et al., 1987). Their data showed that there was little or no measurable uptake of Se by barley leaf and grain at the level of detection (0.05 mg/kg) and there were also no significant increases in chard or radish Se concentrations with sludge addition (0, 45, 90 and 180 mt/ha/year for 9-10 years). Se concentrations in chard were in the range of 0.05-0.11 mg/kg, and 0.17-0.26 mg/kg (dry wt. basis) for radish.

West Side - SJV

Reuse of saline drainage water to irrigate melons and tomatoes caused no loss of yield and no health hazards (Grattan et al., 1987). Both crops accumulate Se when irrigated with Se-containing drainage water (30 to 40 ug Se/L and 200 to 350 ug Se/L, at West Side Field Station, and at Murrieta Farm in Mendota, respectively. The estimated daily intake of Se would be relatively low (6 to 8 ug Se) and was not considered a health hazard by Fan (1986).

Se accumulation and distribution within the plant were reported by Grattan et al. (1987), Ayars et al. (1985) and Ayars and Letey (1987), Burau et al. (1987) and Wan et al. (1987). All found that edible part portions of the plant contained much less total Se than the generally inedible plant parts. The roots contained the highest Se contents.

Another approach of reducing accumulation of Se from soils is by microbial volatilization of Se from soil (Frankenberger, Personal Communication). However, methylation of selenite (selenate) into a volatile form under aerobic soil conditions in the laboratory (Karlson and Frankenberger, In Preparation) is at present a subject of confirmation under field conditions of the west side - SJV.

Information from recently reported research suggests that the previously recommended limit of 20 ug/L for Se in irrigation waters is appropriate general guideline for waters containing very low salt concentrations and essentially no sulfate. Fortunately, these waters usually contain only traces of Se. Selenium is present in shales which also contain soluble salts. If waters have sufficient contact with shales or with soils derived from seleniferous shales to dissolve Se, they will also dissolve the associated sulfate salts. Surface or groundwaters that have not contacted seleniferous shales or soils are likely to have concentrations of Se that can meet this guideline. At a concentration of 20 ug/L the annual input would be 0.2 kg/ha,

assuming water use is 10,000 m^3/ha, which will be within safe limit for Se (in SeO_4 form) as shown by Carter et al. (1969) for alfalfa. However, this limit could be increased for individual crops or for cropping systems if the relationships between Se in the soil solution (Se_{ss}) and Se in harvest products (Se_{hp}) were to be determined so that the maximum Se_{ss} (Se_{ssm}) to protect the users of harvested products could be established.

Carter et al. (1969) reported that 1.0 kg of Se/ha in the form of selenites produced alfalfa that had <4 mg Se/kg of dry weight of forage; however, 1.0 kg of Se/ha in the form of barium selenate produced forage that slightly exceeded the 4 mg/kg level in the first cuttings but not in the second and third cuttings for each of two seasons. The irrigation water in this field research on a silt loam soil in southern Idaho is low in salinity and low in sulfate. The selenate salt was added at one time concentrated in lands at the 15-cm depth, whereas if the Se is added in water it is distributed over the total irrigation season and much more uniformly over the land surface. Because of the well documented effects of lower plant availability of elements broadcast across the land surface as compared to placement in localized bands the 1 kg/ha added in irrigation water should be less available to plants. Application of Se throughout the irrigation season would produce a uniformity of Se in the crop throughout the season. Also, yields of alfalfa are much greater in the SJV than in Idaho because of the differences in growing seasons that provide for three cuttings in Kimberly, Idaho and 5 to 7 cuttings with SJV, thus producing a greater dilution of Se in a larger yield of forage.

The work of Mikklesen et al. (1987) showed that the Se content of alfalfa forage was dramatically reduced in sulfate dominated solution cultures compared to those dominated by chloride. Recent data by Albasel et al. (Part II of this report), that extended the study of Mikklesen into lower Se concentrations and also compared the effects of various ratios of sulfate to chloride on Se uptake, show the large effect of sulfate on reduction in uptake of Se by alfalfa and add additional support for the suggested guideline.

Guidelines

It has been recommended that the Se concentrations in irrigation water not exceed 20 ug/L (National Academy of Sciences, 1973). This guideline was based on assumptions that 1) selenium additions accumulate in the rootzone, 2) forages grown on soils that have accumulated more than 4 kg Se/ha could produce forages containing sufficient Se to cause toxicosis in ruminant animals and 3) annual applications of irrigation water would average 3 acre ft/acre-year. This guideline was recommended for all irrigated lands regardless of soil properties such as acidity-alkalinity and texture, plant species, climate and other water quality characteristics such as sulfate concentration.

The specific conditions for the Westside of the SJV that justify modifying this guideline are:

1. The Se in the waters of the westside is in the form of the selenate ion which is not adsorbed into soil particles and is thus readily leached through and from the soil rootzone.

2. The waters that contain Se are highly saline drainage waters that demand high leaching volumes to prevent salinization of the rootzone, insuring that the added Se will also move on through the rootzone.

3. The waters that contain Se have high concentrations of the sulfate ion which greatly inhibit the absorption of Se by plants.

Guidelines for Se concentrations in irrigation waters should be based on 1) the nature of the soil, 2) the crop to be grown and the uses of its harvested products, 3) climatic factors and 4) other constituents in the water. Soil properties of importance are textural and structural properties that control the ease with which the rootzone can be leached to keep salts and Se from accumulating in the rootzone and chemical properties that might modify the form of Se and its adsorption or desorption. Important crop factors are 1) tolerance of the crop to Se, 2) the accumulation of Se in harvested products used for animal feeds or human foods and 3) tolerance of the crop to salinity and the required leaching fractions that dictate management practices for saline waters. Climatic factors include rainfall, temperature and length of growing season that control crop selection, crop productivity, length of growing season and leaching during rainy seasons. Other constituents or properties of the water that influence the guidelines are total salinity that controls the demand for leaching and limits crop selections and specific ions such as sulfate that inhibit Se absorption and translocation to harvested products.

Meaningful guidelines should thus depend on local conditions. To establish such guidelines we need to know the leachability of the soil, the relationships among Se in the irrigation water, (Se_{iw}), the leaching fraction, (L), that can be obtained with the soil and water management and drainage system, the mean soil solution Se concentration in the rootzone, (Se_{ss}), and the maximum (Se_{ss}) that can be tolerated without exceeding the Se limits in harvested products, (Se_{hp}).

The critical relationships among Se_{ss}, Se_{iw} and L can be calculated from average concentration factors (Fc) for various values of L for ions that are not adsorbed by soil solids. If Se is in the SeO_4 form these relationships can be used because this species is not adsorbed and behaves as a completely leachable anion. Figures 10 and 11 illustrate these relationships. Figure 10 presents the relationship between Se_{ss} and L fractions for a number of Se_{iw} values and Figure 11 presents the relationship between L and Se_{iw} for a number of values of Se_{ss}. To use Figure 11 one needs to know the maximum Se_{ss} that can be tolerated without exceeding Se_{hp} (Se_{ssm}). For example, if Se_{ssm} is 150 ug L^{-1} and Se_{iw} is 75 ug L^{-1} an L value of > 0.3 must be obtained. The Fc values for L values of 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5, respectively, are 5.56, 3.76, 2.58, 2.05, 1.74 and 1.53. These were calculated assuming

Fig. 10. RELATIONSHIP BETWEEN THE AVERAGE CON-
CENTRATION OF Se IN THE SOIL SOLUTION
OF THE ROOT ZONE AND THE LEACHING
FRACTION FOR SIX CONCENTRATIONS OF Se
IN THE IRRIGATION WATER.
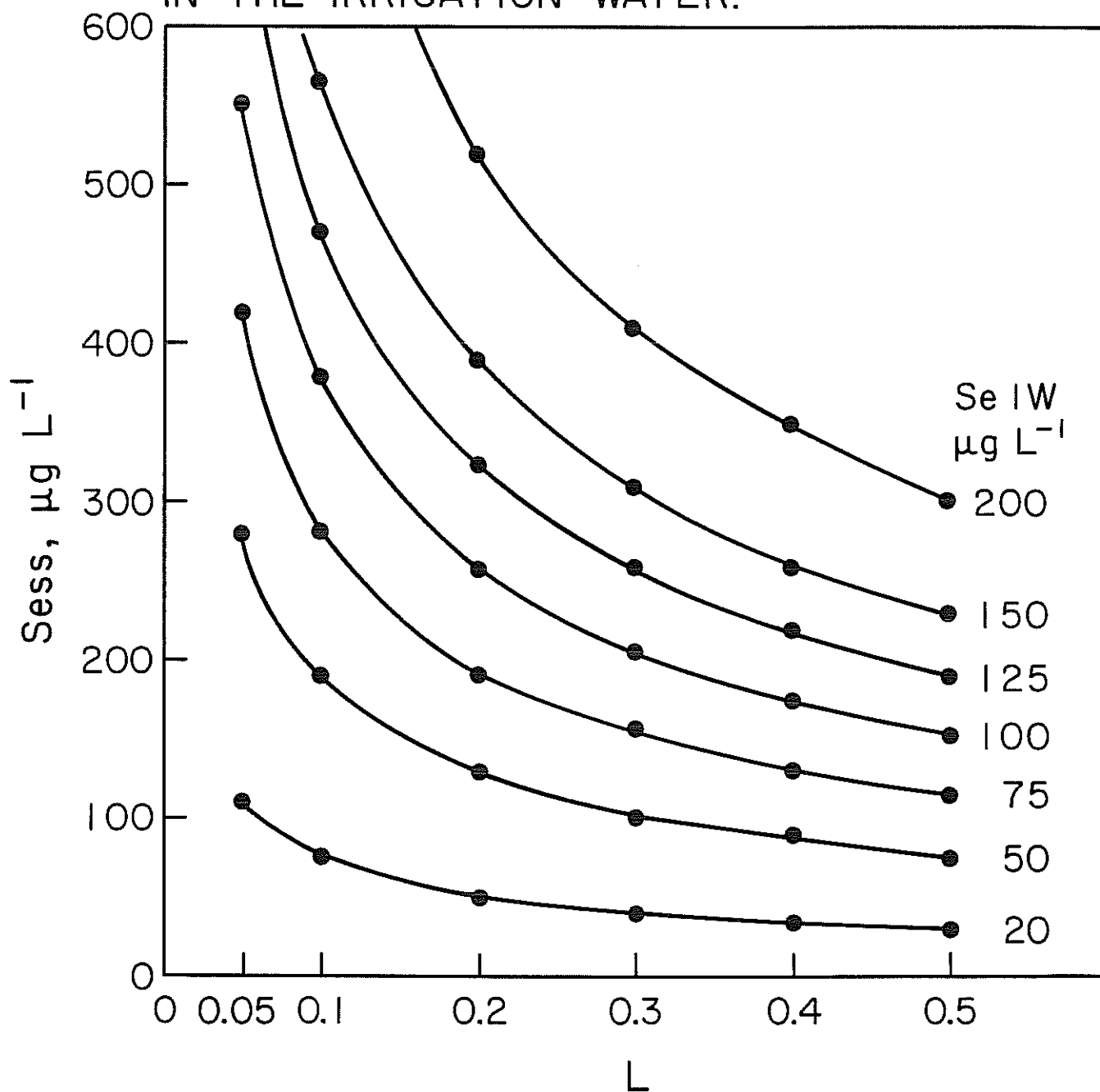
Fig. 11. RELATIONSHIP BETWEEN THE LEACHING FRACTION OF THE SOIL SOLUTION OF THE ROOT ZONE AND THE Se CONCENTRATION IN THE IRRIGATION WATER TO KEEP THE MEAN Se CONCENTRATION IN THE ROOT ZONE TO LESS THAN THE INDICATED VALUES.
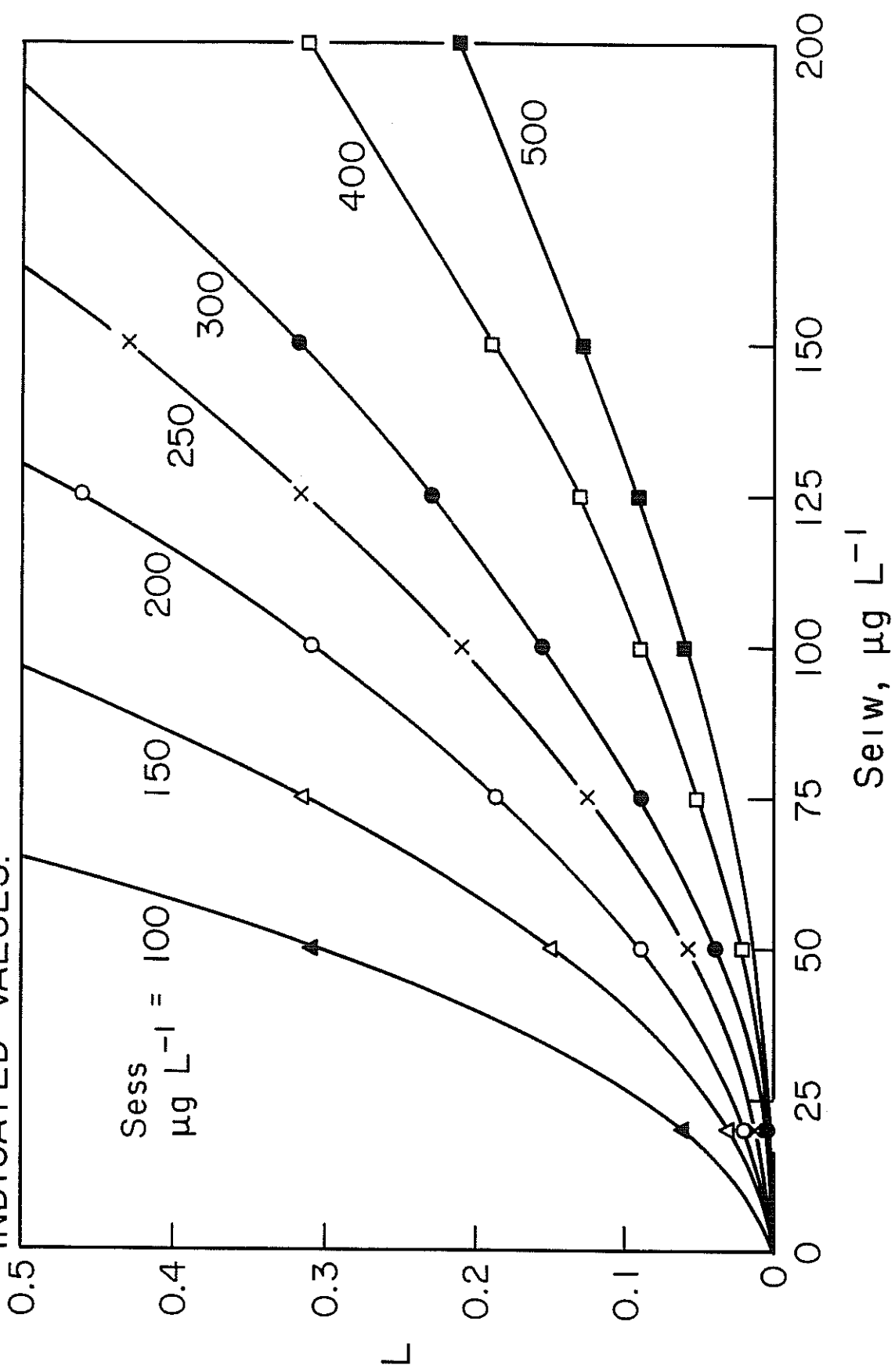
that the water removal from the rootzone was 40, 30, 20 and 10%, respectively, from the first, second, third and fourth quarters of the rootzone.

Research with alfalfa suggest that with saline irrigation waters dominated by sulfate the Se_{ssm} can be set at 250 ug L^{-1} without exceeding the Se_{hp} of 4 mg kg^{-1} which defines the maximum safe Se concentration for feed for bovine animals. The guidelines for Se_{iw} is then dependent on the L that can be achieved with irrigation management for the particular soil being cultivated. If we assume that a leaching fraction of 0.2 or greater will be obtained we can establish a guideline of 100 ug L^{-1} for Se_{iw}. If the soil is highly permeable and has high water transmissivity properties and water management is such that the L value exceeds 0.4 the guideline can be 150 ug L^{-1}. On the other hand, if the land cannot be readily leached a guideline of 50 to 75 ug L^{-1} might be appropriate. As a general rule a successful crop of alfalfa using waters of moderate salinity (EC values of 2 to 4 dS/m^{-1}) will require leaching fractions of 0.2 to 0.4 so that a general guideline of 100 mg L^{-1} for alfalfa seems reasonable. Because alfalfa is the most sensitive irrigated crop on the West Side of the SJV for Se accumulation in relation to the use of the harvested product, the general guideline for all irrigated agriculture using sulfate dominated saline waters that require leaching fractions of >0.2 should be established as 100 ug L^{-1} or less. This guideline provides a margin of safety for all less sensitive crops.

MOLYBDENUM

Introduction

Molybdenum is an important industrial element. It is also an essential metallic cofactor in animal and plant enzymes. At high concentrations in forage it can be toxic to ruminant animals. The range between toxicity and deficiency in animals is narrow and therefore careful control of Mo in animal diets is essential.

The coordination number of Mo is four, as in MoO_4 (Killefer and Linz, 1952). At moderate to high concentrations in solution, molybdate readily polymerizes into polymolybdates with a wide variety of very complex structures. In dilute solution such as that found in soils or in most natural waters, the predominant form of Mo in solution is the molybdate anion (MoO_4^{2-}).

A review of literature dealing with Mo in soils and in plant and animal nutrition prior to 1956 was published in a special issue of Soil Science (Bear, 1956). Reviews of the inorganic chemistry of Mo have been published by Killefer and Linz (1952), Northcott (1956), and Elwell and Wood (1971). The agricultural importance of Mo has been discussed (Mortvedt et al., 1972) and various aspects of Mo in the environment have been published in the proceedings of an international symposium on "Molybdenum in the Environment" (Chappell and Peterson, 1977). Underwood (1977) and Beeson and Matrone (1976) reviewed the biochemical importance of Mo in animal and human nutrition. Recently a condition known as genu valgum affecting young people in parts of India has been attributed to excessive intakes of Mo and F (Agrawal, 1975).

There appear to be no clear-cut instances in which Mo can be regarded as an essential trace element for human beings. However, one very important beneficial role of Mo has been suggested, and that is the ability to reduce the incidence of dental cavities in human beings (Pienaar and Bartel, 1968; Adkins and Losee, 1970; Glass et al., 1973).

It has generally been considered that Mo is not a serious environmental contaminant in terms of human health. The U.S. Food and Drug Administration lists Mo among the "relatively harmless" metals, the safest class of metals.

Natural Occurrence

Molybdenum occurs in soils in primary minerals, clay minerals, associated with sesquioxides, water-soluble Mo, and organically-bound Mo.

In primary minerals Mo is known to exhibit both chalcophil and lithophil properties. Its chalcophilic properties are expressed by its occurrence in association with sulphur as the mineral molybdenite

(MoS_2). Its lithophilic characteristics are revealed by its presence in silicate structures where it may occur as a guest element in feldspars and micas. Substitution of Mo^{4+} for Al^{3+} is presumed. It may also occur in oxy-anion form in such minerals as powellite ($CaMoO_4$), wulfenite ($PbMoO_4$), and ferromolybdite ($Fe(MoO_4)_3 \cdot 8H_2O$). Molybdenum held in primary mineral structures is only sparingly soluble and requires relatively drastic treatments such as fusion or digestion with strong acids to effect appreciable solution.
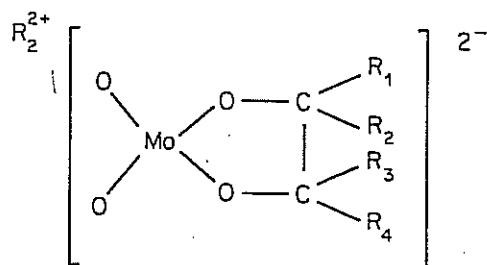
Molybdenum, adsorbed as molybdate (MoO_4^{2-}) on the surface of clay or secondary minerals, is less firmly bound and may be removed by conventional extracting solutions. Such Mo is usually categorized as 'available' but its availability depends to a greater or lesser degree on pH and phosphate status (Davies, 1956).

In acid soils much of the Mo may be associated with sesquioxides, especially iron oxides. The binding here is quite firm and in some classically Mo-deficient soils total contents may be relatively large but fixation by iron oxides renders the Mo unavailable to plants.

The nature of this binding has been studied (Jones, 1957; Reisenauer et al., 1962; Mikhailov, 1962) and it is probable that initial ferromolybdite phases eventually transform to more usual iron oxide minerals such as goethite and hematite with Mo^{4+} substituting for Fe^{3+}.

Water-soluble Mo in soils is generally quite low ($\leq$ 0.1 mg/L or less) and is very much pH dependent. The concentration of Mo in soil water is largely controlled by the adsorption of MoO_4^{2-} on Fe_2O_3 and only under alkaline conditions does the fraction assume any worthwhile proportions. Such conditions were found by Barshad (1951a) where water-soluble Mo values ranged from 0.8 to 3.9 mg/L.

Less would appear to be known concerning the complexes formed when Mo is in organic combination than when it is inorganically bound. The presence of high levels in plants under acid soil conditions is seen by Mitchell (1964) as evidence of organically bound — and plant available — Mo. It is suggested that chelation has 'protected' the Mo from entry into the more insoluble compounds that reduce availability in acid conditions. Manskaya and Drosdova (1968) suggest that the reaction between Mo and humic acid may be similar to that between it and polyhydric phenols such as pyrocatechol and pyrogallol. It has also been demonstrated (Spengler and Gansheimer, 1957) that Mo forms water-soluble complexes with organic compounds having <u>ortho</u> hydroxyl groups. Such compounds would include alcohols, phenols, hydroxy acids, and organic monobasic acids. The structure proposed for these complexes is as follows:

$$R_2^{2+} \quad \left[\begin{array}{c} O \\ \backslash \\ Mo \\ / \\ O \end{array} \begin{array}{c} O - C \Big\langle \begin{array}{c} R_1 \\ R_2 \end{array} \\ \Big| \\ O - C \Big\langle \begin{array}{c} R_3 \\ R_4 \end{array} \end{array} \right]^{2-}$$

These complexes form insoluble salts with metallic cations.

Because Mo combines with a number of organic substances of the organic fraction of soils, it will be in a continual state of circulation as a result of immobilization and mobilization.

Molybdenum contents of soils are very dependent on the Mo-content of parent material (Massey et al., 1967) and are usually greater than that of the parent material (Aubert and Pinta, 1977). Molybdenum accumulates in the upper "humiferous" zone of the soil because it is fixed by soil organic matter (Aubert and Pinta, 1977). An alternative explanation is that the inorganic soil constituents in the surface are more weathered and adsorb the Mo. Because Mo accumulates in soils, it has been used as an indicator element for geothermal prospecting, both for Mo ores and for the copper minerals with which it is sometimes associated. In fact, both Mo levels in water and Mo levels in soils and plants (Webb et al., 1968; Thomson et al., 1972) have been used as indicators of high Mo parent materials.

The total concentration of Mo in soils averages 1 to 2 mg/kg, but may reach concentrations as high as 24 mg/kg (Allaway, 1968; Page, 1974; Aubert and Pinta, 1977). Most reports have associated high Mo concentrations in soils with sedimentary parent materials, especially shales (Swaine and Mitchell, 1960). Aubert and Pinta (1977) report that ancient alluvial sands and sandy loams from Bierlorussia contained 0.28 to 0.90 mg Mo/kg, morainic clay loams and loessic loams had 0.9 to 4.9 mg Mo/kg, and clays averaged 2.8 to 3.7 mg Mo/kg. Barshad (1948) reported values of total soil Mo ranging from 0.1 to 9.7 mg Mo/kg in soils from 20 different locations in California.

Factors Affecting Availability

It is well recognized that liming acid soils increases Mo availability and numerous studies testify to this effect (Anderson and Moye, 1952; Davies, 1956; Stout and Johnson, 1956; Scott, 1963; Widdowson and Walker, 1971; Cheng and Ouellete, 1973). The magnitude of the liming effect can vary appreciably among soils, depending on the Mo forms

present. An anion exchange, involving the replacement of MoO_4^{2-} by OH^- is assumed to be the mechanism for increased Mo availability following liming. Liming effects on Mo availability are smaller when it is present in organic combination (Mitchell, 1972). Chelation would appear to lessen the possibility of MoO_4-OH-type reactions occurring with a resultant decrease in Mo release.

Molybdenum has not been found to precipitate as a calcium molybdate at high soil pH. Its availability to most plants reaches a maximum the near neutrality and does not diminish as pH increases (Lindsay, 1972).

The behavior of Mo in soils has been extensively studied because it has a rather unique position among other micronutrients in that it is least soluble in acid soils and is readily mobilized in alkaline soils. Vlek and Lindsay (1977) concluded that soil solubility of Mo is very close to that of $PbMoO_4$-soil-Pb systems. Molybdenum from wet alkaline soils such as SJV, west side soils, is most easily taken up, but the geochemical processes involved in this phenomenon are not completely understood. Apparently, this uptake is related to the high activity of MoO_4^{-2} in alkaline medium, as well as to an ability to form soluble thiomolybdates under reducing conditions (e.g., MoS_4^{2-}, $MoO_2S_2^{2-}$).

Molybdenum solubility in soils increases as a function of hydroxyl concentration, following the proposed simplified reaction (Barshad, 1951a; Lindsay, 1972):

$$MoO_4^- + Soil \begin{matrix} OH \\ \\ OH \end{matrix} \rightleftharpoons Soil-MoO_4 + 2OH^-$$
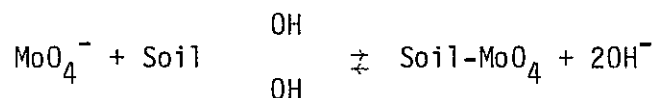
Reisenauer et al. (1962) developed an equation which related Mo sorption to pH for a given soil or mineral adsorber.

The availability of Mo from organic matter complexes is a function of the method of binding. The form in which it is complexed is not as yet fully understood although organic compounds with hydroxyl groups in the ortho position to one another seem to have a particular affinity for the element (Manskaya and Drosdova, 1968).

Soil reaction and drainage are important; Mo deficiency occurs on acid sphagnum peats while toxic pastures are frequently associated with poorly drained alkaline soils rich in organic matter. This point is illustrated by the data of Table 1 (Fleming, 1973). The soils highest in available Mo are poorest in drainage, slightly more alkaline in reaction, and highest in organic matter. The point must also be made that no concepts of the effect of organic matter on Mo availability can be considered complete without consideration of the microbiological factors involved.

Poorly drained soils are frequently associated with excess Mo in herbage (Ferguson et al., 1943; Kubota et al., 1961). The data of Table 1 also illustrate this point clearly but as has been pointed out there existed in this case concomitant effects of increased pH and organic matter accumulation. This enhanced solubility under reducing conditions is at variance with the work of Amin and Joham (1958) and Lindsay (1979). These workers have shown that Mo in the more highly oxidized state of MoO_3 was stable.

Table 1. Effect of Drainage on Availability of Soil Molybde- num (Fleming, 1973). (Reproduced by permission of Academic Press Inc. (London) Ltd.)

Drainage	Org.C (%)	pH	Mean Mo content (ppm) Soil[*]	Herbage
Freely drained	4.0	6.5	0.39	3.1
Poorly drained	6.4	6.5	0.44	3.9
Very poorly drained	10.7	6.6	2.36	13.0

[*]Grigg, 1953.

Other factors may influence Mo uptake to some extent thereby causing concentrations in plants to vary somewhat from year to year, e.g., soil moisture content and drainage (Kubota et al., 1963). A high P availability is believed to enhance Mo solubility (Karimian and Cox, 1978) and uptake by plants (Gupta and Lipsett, 1981).

A possible explanation of the drainage effect on micronutrient solubility in general may be found by considering the influence of anaerobic conditions on microbial decomposition of organic matter.

Molybdenum in Waters

Molybdenum has been found in many surface and groundwaters, although in numerous instances it has been below detection limits of the analytical method employed. In general, concentrations in water are found to be in the range of a few ug Mo/L.

Livingstone (1963) surveyed data on the chemical composition of waters around the world. He reported that concentrations as high as 6.9 ug Mo/L were measured in river waters from Azerbaidshan S.S.R. Lake water samples from Maine (U.S.A.) contained as much as 2.5 ug Mo/L, with a mean of 0.023 ug Mo/L. Major rivers of North America had concentrations as high as 6.9 ug Mo/L; over half the samples contained undetectable quantities of Mo.

Hem (1970) reported an average of 0.68 ug Mo/L for surface waters of the U.S.A. Kopp and Kroner (1970) measured the trace element content of 1,577 samples of surface waters collected from 15 geographically diverse areas of the U.S.A. (Table 2, Jarrell et al., 1980). Only 516 samples (33% of the total number) contained Mo at concentrations greater than detection limits. Maximum concentrations ranged from 53 to 1,100 ug Mo/L depending upon the geographical region. Apparently the detection limits for Kopp and Kroner's work were much higher than others who recorded lower average values for Mo concentrations.

Sugarawa (cited by Turekian, 1971) presented data on the average chemical composition of river waters and atmospheric precipitation in Japan. The average concentration of Mo in river waters from Japan was 10 times higher than that of atmospheric precipitation (0.6 and 0.06 ug Mo/L, respectively).

Val'Chuk and Chipik (1974) found that the Mo content of well water was roughly correlated with the Mo content of plants from the area around the well. Molybdenum levels in the well waters were found to vary greatly over short distances.

The average Mo concentration in sea water, as reported by Hem (1985), is 10 ug/L. Based upon radioactivity estimates (99Mo, half-life 66 hr), Rice and Wolfe (1971) showed literature data indicating that Mo is distributed in sea water in the ionic, colloidal, and particulate physical states at 30, 10, and 60%, respectively.

Masironi (cited by Andelman, 1973) reported a strong positive correlation ($r = 0.91$) between the levels of Mo and water hardness in 116 samples in river waters of the U.S.A. Andelman (1973) indicated that such a relationship is expected on the basis of the fact that weathering of limestone and other calcium- (and magnesium-) bearing minerals exposes quantities of trace elements which can be leached. The high pH of these waters should also increase the solubility of Mo.

Kim and Martin (1974) measured positive correlations between the concentration of Mo in Florida's Peace River, and its humic and fulvic acid content; trace metals, especially iron; and orthophosphate; as well as rainfall and mean river discharge.

Results reported by LeGendre and Runnells (1975) on the removal of dissolved Mo from wastewaters by adsorption or co-precipitation with solid ferric iron oxyhydroxides at low pH. A significant increase from 4.3 to 7.2 ppm of Mo concentrations in alfalfa and available soil Mo was observed at one site irrigated with water containing 213 ppb Mo (Jackson et al., 1975). This level, however, is below the 10 ppm level considered toxic to livestock.

Table 2. Concentration of Mo in surface waters in the U.S.A.*

	No. of sample stations	No. of rivers	No. of samples analyzed	Samples with detectable Mo (%)	Detection limit (ug/L)	Maximum concentration found (ug/L)
Northeast	8	6	91	13	4	61
North Atlantic	10	5	171	33	4	168
Southeast	10	7	91	19	2	53
Tennessee River	6	2	68	38	3	67
Ohio River	13	7	242	28	6	473
Lake Erie	2	2	47	28	21	108
Upper Mississippi	10	4	112	69	4	360
Western Great Lakes	6	3	66	52	4	129
Missouri River	15	8	147	32	8	354
Southwest-Lower Mississippi	17	5	155	20	11	1,100
Colorado River	8	4	100	37	10	444
Western Gulf	5	2	47	11	4	59
Pacific Northwest	14	7	162	39	2	128
California	3	3	29	38	14	124
Great Basin	2	2	19	58	3	338
All waters	129	67	1,577	20	21	1,100

*From Kopp and Kroner (1970).

Molybdenum in Plant Nutrition

Molybdenum's most important functions in crop plants are associated with nitrogen metabolism (Schneider, 1976; Spence, 1976). Its role is primarily that of an enzyme activator (Table 3). Molybdenum is required by all plants when nitrogen is absorbed in the nitrate form, because it is a critical constituent of the nitrate reductase molecule. Nitrate reductase catalyzes the biological reduction of NO_3^- to NO_2^-. Different crops have widely varying Mo requirements as reported by different workers. In general, legumes have a Mo requirement 2 to 3 times greater than that of nonlegumes (Table 4, Johnson, 1966).

Table 3. Molybdenum containing enzymes in plant nutrition.

Enzyme	Substrate
Nitrogenase (plant)	N_2
Nitrate reductase (plant)	NO_3^-
Sulfite oxidase (animal)	SO_3^{2-}
Aldehyde oxidase (animal)	Aldehydes
Xanthine dehydrogenase (animal)	Purines
Xanthine oxidase (animal)	Purines

Molybdenum toxicity is modified by other dietary components with the effects not clearly defined. Although the research data are somewhat conflicting, generally it appears that at least a normal level of sulfate provides some protection against high Mo in plant by increasing excretion (Cunningham et al., 1959; Underwood, 1977; Vanderveer and Keener, 1964). Naturally occurring Mo in pastures often appears to be much more toxic than a similar amount of experimentally added Mo (Cunningham, 1950; Vanderveen and Keener, 1964). The maximum amount of molybdenum that could normally be consumed without toxicity for ruminants is about 6 mg/kg in the dry matter (dry wt.) of the diet. However, under some conditions substantially more can be fed without adverse effects (National Academy of Sciences, 1978).

Page et al. (1979) reported that plant Mo was increased by increasing the content of fly ash in soil. Also, the authors noticed decreased concentrations of Mo in the plant tissue in successive cuttings of the forage crops. Cope (1962) and Doran and Martens (1972) pointed out that application of high amounts of coal ash and fly ash to soil could result in forage that contains toxic amounts of Mo.

Plant requirements for Mo have not been established (National Academy of Sciences, 1984). An exact estimate of the Mo requirement

Table 4. Molybdenum requirements of selected leguminous and non-leguminous plants.[a]

Crop (Scientific name)	Type of plant	Concentration in plant showing deficiency (mg Mo/kg dry matter)
Alfalfa (Medicago sativa)	legume	0.28
Clover (Trifolium repens)	legume	0.15
Broccoli (Brassica oleraceae)	non-legume	0.04
Citrus-orange (Citrus sinensis)	non-legume	0.03-0.08
Spinach (Spinacia oleracea)	non-legume	0.10
Tomato (Lycopersicon esculentum)	non-legume	0.13
Turnip (Brassica rapa)	non-legume	0.03

[a]Data extracted by Johnson (1966) from several literature sources.

is impossible since copper and sulfate alter Mo metabolism. Furthermore, the majority of research on molybdenum has concentrated on the interrelationship with copper and sulfate, rather than on a specific requirement. Ward (1978) speculated that there is no safe dietary level of Mo because of such interactions.

Molybdenum levels of 5 to 6 ppm (dry wt. basis) inhibit copper storage and produce signs of molybdenosis (National Academy of Sciences, 1980). Elevated dietary copper alleviates the toxic effects of Mo (Ferguson et al., 1943; Miller and Engel, 1960; Mills, 1960; Vlek and Lindsay, 1977; Ward, 1978).

The use of sulfate or manganese fertilizers may help to reduce Mo uptake (Johnson, 1966).

Nutritional interest in Mo is overwhelmingly concerned with plant concentrations and their toxic effects on animals and their interactions with Cu and SO_4^{2-}. The effect on animals of high Mo intake depends on the species and age of the animal, the amount and chemical form of the Mo, the Cu status and intake, the inorganic sulfate and total S content of the diet and to dietary contents of substances as protein, cystine and methionine capable of oxidation to SO_4^{2-} in the body, and with the level of intake of other metals such as Zn and Pb (Underwood, 1976).

Miltimore and Mason (1971) claim that the critical Cu/Mo in animal feeds is 2.0 and that feeds or pastures with lower ratios would be expected to result in conditioned Cu deficiency. The results of a study of English pastures also indicate the importance of the Cu/Mo ratio to the incidence of hypocuprosis in sheep, but with a critical ratio closer to 4.0. Suttle (1973) indicates that Mo can interfere with Cu metabolism at dietary levels of Mo concentrations below 5 ppm. But in laboratory experiments Mo interfered with Cu at Mo concentrations both below and above 5 ppm.

Molybdenum toxicity in ruminants is generally considered to be a Mo-induced copper deficiency (Underwood, 1976). The influence of sulfate on Cu-Mo interactions in ruminants has been noted (Clawson, 1972). Molybdenosis is commonly treated with dietary copper sulfate or injections of Cu-glycinate (Clawson, 1972). This problem, however, is characterized by severe diarrhea, and the loss of general health of the animals. The relative tolerance to excessive Mo level in the plants is determined on the basis of copper level (Arthur, 1965; Vanderveer and Keener, 1964) and to some extent on the basis of sulphate sulphur level (Huber et al., 1971). The upper limit of Mo in plants at which it becomes toxic to animals is thus raised under adequate Cu and S levels. Molybdenum has been identified as an element posing as a potentially serious hazard when municipal sewage sludge is applied to agricultural land (CAST, 1976), but there have been surprisingly few reports on Mo uptake from sewage sludge-treated soils particularly under field experimental conditions. Jarrell et al. (1980) and Williams and Gogna (1981) reported that sludge applications resulted in increased content of Mo in plants grown under greenhouse conditions.

Adsorption of Molybdenum in Soils

Considerable research has been carried out to characterize the mode of Mo adsorption by various soils and soil minerals. The role of Fe(III) oxides and hydroxides as a Mo adsorbent in soils has been emphasized by several investigators (Jones, 1956; Reisenauer et al., 1962; Mikhailov, 1962; Reyes and Jurinak, 1967; and Taylor and Giles, 1970). Other Mo-sorbing minerals in soils that have been given some attention are metahalloysite, nontronite, kaolinite (Jones, 1957), illite and allophanes (Theng, 1971), and oxides of titanium and aluminum (Reisenauer et al., 1962). Others consider soil organic matter as an important adsorbent for Mo in humus-rich soils (Tuev et al., 1965; and Szilagyi, 1967).

Each of these soil constituents is thought to form covalent bonds to some degree with Mo ions (Wakatsuki and Furukawa, 1974). This process, known as specific adsorption, can be studied by Langmuir (1918) and Freundlich (1926) adsorption isotherms. The Langmuir equation is based on the kinetic theory of gaseous adsorption onto solids, but is often used to relate the adsorption of ions from solution (Ellis and Knezek, 1972). The Freundlich equation has no sound theoretical basis, but is an empirical relationship used to describe the adsorption of ions or molecules from a liquid onto a solid phase.

Reisenauer and others (1962) found that adsorption of molybdate onto soils at a fixed pH followed the Freundlich equation. Reyes and Jurinak (1967) and Theng (1971), in studying Mo adsorption onto hematite and soil at pH 4.0, found two adsorption reactions, each conforming to a Langmuir isotherm. The isotherms were interpreted as showing two energetically distinct binding sites for Mo.

Molybdenum adsorption depends not only on the kind of adsorbent, but also on the pH of the system. Since H^+ and OH^- are considered potential determining ions, they cause a change in surface potentials of minerals with pH. Hingston et al. (1970) showed that capacity of an adsorbent for binding Mo is pH dependent and that an adsorption maximum occurs at pH = pK_2 (~4). Indeed, Jones (1957) and Theng (1971) found maximum retention of Mo by soils, clay minerals, or sesquioxides at pH 4. Reyes and Jurinak (1967) demonstrated that the adsorption maximum of molybdate on hematite was reduced by 80% if the pH was changed from 4.0 to 7.75. The zero point of charge of the hematite sample occurred at pH 8.0.

Molybdenum Availability to Forage Plants

The availability of soil Mo to plants varies significantly, and is dependent on soil as well as plant parameters. The uptake of Mo is well correlated with the amount of Mo in the soil solution (Evans et al., 1950), which ranges from $10^{-8}M$ in low Mo soils (Lavy and Barber, 1964) to $10^{-5}M$ in soils producing toxic herbage (Kubota et al., 1963). Soil parameters affecting Mo solubility include pH, mineralogy, degree of Mo

saturation, and presence of competing anions such as phosphate and sulfate (Reisenauer, 1967; Davies, 1956).

The pH dependence of Mo availability was recognized by Lewis (1943), who showed that basic fertilizers increased the uptake of Mo by grasses growing on acid soils. Ahlrichs et al. (1963), James et al. (1968), and Gupta (1969, 1970) reported increased contents of Mo in alfalfa after liming. Barshad (1948) found that acidifying alkaline soils greatly reduced water-soluble Mo. Knowledge of the Mo status of soils can help explain effects of Mo fertilization and contamination on the molybdenum uptake by plants (Ahlrichs et al., 1963; James et al., 1968; Cunningham and Hogan, 1949; Reisenauer, 1956; and Gupta and Mackay, 1968).

Molybdenum concentrations in plants are usually less than 2 mg/kg (dry wt. basis); hence, a low uptake rate should supply the plant requirement. The Mo requirement is much greater for legumes, because it is used in the nodule for nitrogen fixation, and levels needed for plant growth are much lower than levels needed to supply the root nodule with sufficient Mo for nitrogen fixation. Hence, most plant species showing responses to Mo fertilization are legumes.

Molybdenum concentrations in plants that are adequately supplied with Mo range from 1 to 2 mg/kg; with higher rates of molybdenum supply, however, plant concentrations can be as high as 20 mg/kg (dry wt. basis). This increase without a corresponding increase in plant growth indicates that there is a wide range of Mo concentrations over which Mo absorption increases concentration of Mo in the plant. Hence the influx versus concentration relation may be approximately linear in soil systems.

Stout et al. (1951) found that adding sulfate depressed Mo uptake, possibly because sulfate and Mo compete for the same absorption sites on the root, whereas adding phosphate stimulated Mo uptake in solution culture. Enhancement with phosphate was not explained. The same researchers also found that increasing solution pH depressed Mo uptake according to the relation shown in Fig. 12. This effect on Mo adsorption is the opposite of that occurring in soil systems. In soil, the effect of pH on Mo levels in the soil solution overshadows the effect of solution pH in depressing Mo-absorption rate.
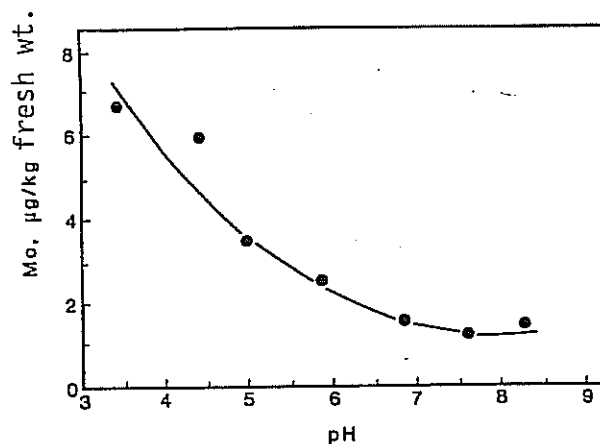
FIGURE 12. Effect of solution pH on absorption of molybdenum by tomato from solution culture. Reprinted from Stout et al. (1951) by permission of Martinus Nijhoff Publishers B. V.

In irrigated agriculture, it has been recommended that concentrations of Mo not exceed 0.01 mg/L in the water for continuous application on all soils, or 0.05 mg/L for short-term use on soils that react with Mo (National Academy of Sciences, 1973). These values are apparently based on previous studies which showed that levels of Mo greater than 0.01 to 0.1 mg/L in saturation extracts of soil were associated with toxicity to animals. The validity of these studies to establish irrigation water criteria for Mo was, however, questioned by Jackson et al. (1975). They maintained that concentrations of Mo in the soil solutions are determined by the labile pool of Mo in the soil. A simulation model study by these authors indicated that 0.4 mg/L Mo in irrigation water uniformly distributed in soil to a depth of 1.5 m with 40% retention of Mo would result in toxic levels of Mo in plants within 3 yr.

A lime-treated sludge increased Mo concentration in plant tissues after several years of sludge application (Soon and Bates, 1985). The increase in plant Mo concentration was highest in the eighth year and last year of the experiment, also the soil-sludge interactions contributing to increased Mo uptake. However, the results indicate that there is not a significant problem in the utilization of sewage sludge on agricultural land, provided that sludge guideline (Alberta Environment, 1982) are followed, i.e., modest rates of sludges containing low-to-medium concentrations of metals and other toxic elements are used.

Leaching Losses of Molybdenum

In soils exhibiting a net downward movement of water, soluble Mo may be lost from the soil profile by leaching. From geochemical studies it appears that Mo tends to be concentrated in topsoils derived from igneous rocks, indicating the resistance of this element to leaching as bases are removed (Wells, 1960). In alkaline soils, Mo is more mobile, and if not leached from the profile by rain or irrigation water, the Mo is highly available to plants (Johnson et al., 1952; Muller et al., 1964).

Jones and Bellings (1967), employing columns of soil under excessive precipitation, found that Mo leached through most soils, particularly soils of alkaline reaction, but some accumulation by adsorption of Mo occurred in the top 2 inches of the alkaline soils. Pratt and Bair (1964) using lysimeters to measure the net change of Mo found that with a leaching fraction of 7% to 8%, the Mo accumulation was about three-fourths of the amount added in the irrigation water.

Guidelines

The approach used for arriving at recommended guidelines for Se in irrigation waters assumed that the Se in waters is in the SeO_4 form which is not adsorbed by soils and thus moves through the soil with drainage waters and that it is concentrated in the soil solution as water is lost by evapotranspiration in the same manner as the chloride ion. Because Mo is adsorbed by soils the approach to establishing guidelines must be modified to include adsorption and desorption processes which can be described by the relationships between amount of Mo adsorbed per unit weight of soil and the concentration of Mo in the soil solution (Fig. 13). As increasing quantities of Mo are added the adsorption capacity represented by X/M must be satisfied before the concentration, C, can be attained. If additions of Mo are stopped an amount of Mo must be desorbed to attain a lower concentration. Desorption can result from removal of Mo by plant roots from the solution or by leaching in drainage water. The adsorption-desorption processes buffer the soil system against rapid changes in Mo concentrations. If a water containing a higher Mo concentration, compared to the previously used water, is introduced, time will be required for the amount of Mo to be added to satisfy the adsorption capacity and allow the concentration in the soil solution to reflect the Mo concentration in the water. Thus, to establish a guideline one must know the quantities of Mo added, the concentration in the water and rates of removal in drainage waters and in harvested plants extrapolated over a period of time in years or decades.

Another way of presenting the adsorption-desorption processes is through the following general equations:

$$\text{Soil Solution Mo} \rightleftarrows \text{Labile Mo} \rightleftarrows \text{Residual Mo}$$

The soil solution Mo is available to plants and moves with the soil water. The labile Mo is the adsorbed form that increases or decreases as the soil solution Mo increases or decreases. The residual Mo is extremely insoluble and unavailable. Conversions of residual Mo to labile Mo and from labile to residual forms are slow processes.

To maintain a permanent irrigated agriculture the input of Mo in irrigation water must be balanced by outputs at a level of available Mo in the soil that is below the threshold for adverse effects on crops and animals. The outputs are removal in harvested crops, leaching beyond the rootzone and conversion in the soil to residual forms.

There is a paucity of data from long-term experiments relating Mo inputs to the toxicity of Mo to plants or to animals that consume forages and grains. What little information that is available suggests that for the protection of bovine animals that consume alfalfa hay the maximum Mo concentration should not exceed 50 ug/L for waters used on the west side of the SJV. The Mo input for this concentration assuming an annual water application of 10,000 m^3/ha will be 0.5 kg/ha. In making this recommendation we are assuming that the sum of removals in crops, leaching losses and conversions in the soil to residual or unavailable forms will in the long term equal the inputs. From the research of Vlek and Lindsay (1977) we feel that this recommended maximum concentration will provide protection for a number of decades if not indefinitely. As more research is completed this recommendation can be adjusted.

The recommended maximum concentration of Mo in irrigation waters used on many crops could be increased substantially without any adverse effects. However, the accumulated Mo in an adsorbed or labile form could restrict the crop selection during the period of time required for desorption and removal by leaching. Thus, for general agricultural use over a long period of time the guideline should provide protection for the most sensitive situation which is the production of forage crops for livestock consumption.

Fig. 13. RELATIONSHIP BETWEEN AMOUNT OF Mo ADSORBED BY THE SOIL PER UNIT WEIGHT OF SOILS, X/M, AND THE CONCENTRATION OF Mo IN THE SOIL SOLUTION, C.
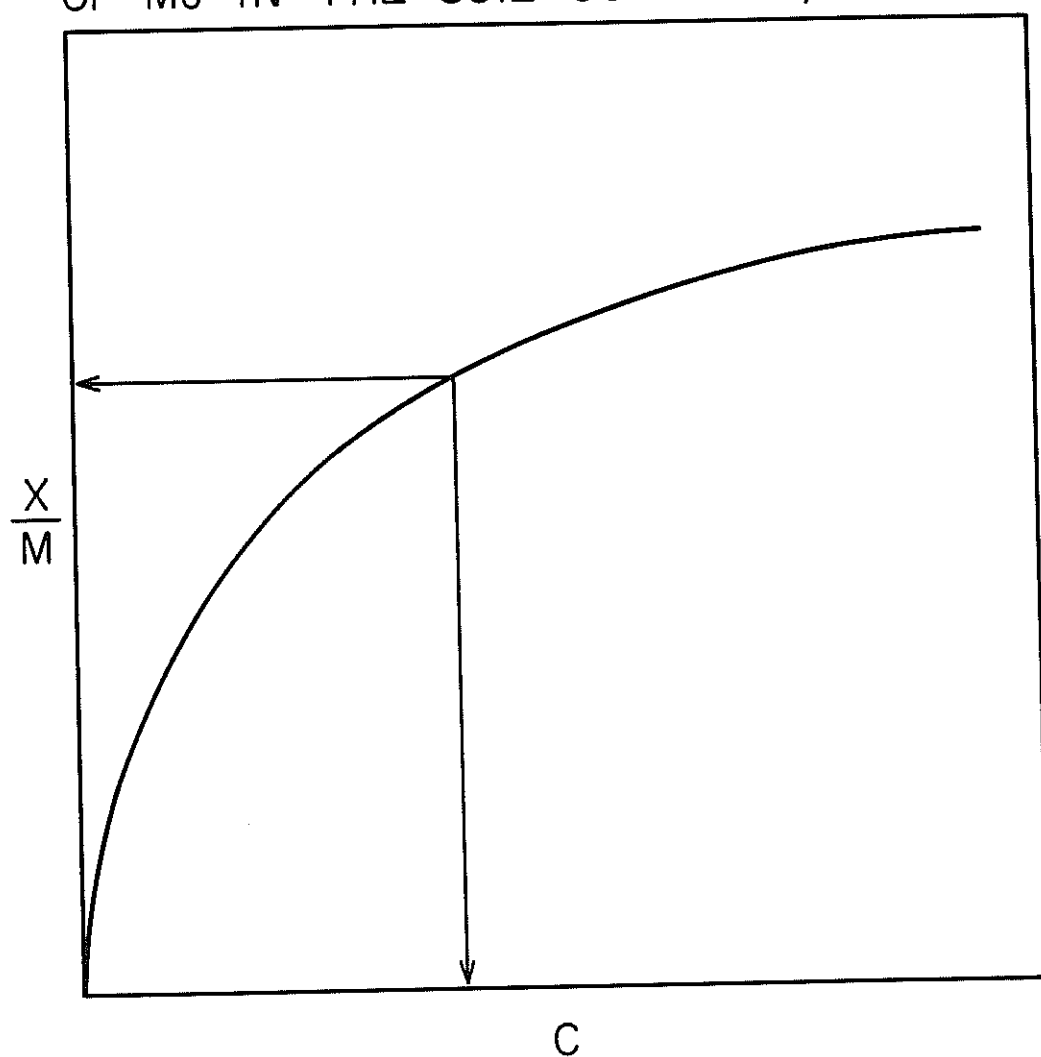
ARSENIC

Introduction

The As content of normal soils are reported to range from 0.1 to about 50 ppm and average 5 ppm (Hawkes and Webb, 1962). Arsenic levels in the foliage of most plant species generally do not exceed 10 ppm and are usually 5 ppm (dry wt. basis) or less (Williams and Whetstone, 1940). Temple et al. (1977) reported that plants growing on soil with As contents in excess of 1500 to 2000 ppm total As also appeared to be visibly unaffected.

Clements and Munson (1947), and Dorman and Coleman (1939) show that the amounts of total As that will produce the initiation of toxicity varies with soil texture and other factors that influence the adsorptive capacity. Data from Crafts and Rosenfels (1939) for 80 soils showed that for a 50 percent yield reduction with barley, 120, 190, 230 and 290 pounds As per acre were required for sandy loams, loams, clay loams and clays, respectively.

The sorption capacity of a soil is affected by the texture, sesqui-oxide content and the presence of other interfering elements. Sand and silt fractions show little arsenic sorption capacity due to the low surface area and the predominance of quartz (Dickens and Hiltbold, 1967) while the clay fraction is the main sorber (Johnson and Hiltbold, 1969; Jacobs et al., 1970 a&b).

The influence of the clay fraction on As sorption can be seen in Fig. 14. Arsenic occurs in the environment in a wide variety of relatively stable chemical forms. Its two primary oxidation states are As(III) and As(V). In nature the primary inorganic forms are pentavalent, though trivalent compounds are readily found in water, particularly under anaerobic conditions (Hammond and Foules, 1986).
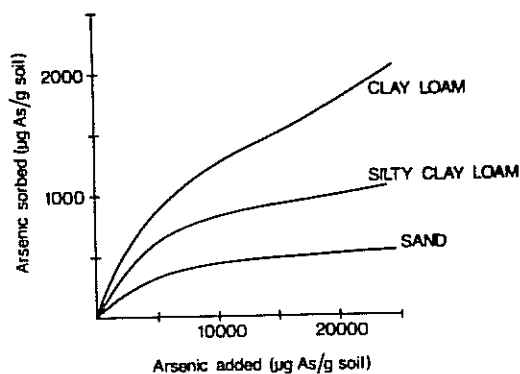

Fig. 14. The sorption of arsenic by different soils. (Modified from Jacobs et al., 1970b.)

Arsenic in Plants

Plant accumulation of As can be affected by many factors, including plant species, type of compound and method of application, soil conditions and fertilizer application. It is rare that As accumulations in plants reach levels that are harmful to animals and man because invariably, growth is reduced before the content will reach toxic levels. This was shown by Woolson (1973) who calculated the values in crops that would occur when their growth had been reduced by 50% (GR^{50}). The contents (Table 6) were calculated from regression equations of available As in the soil on crop As content and growth. It is unlikely that farmers could economically harvest a crop with such a reduction in yield; therefore levels of this kind are infrequent.

Table 6. Arsenic contents of crops at a growth reduction of 50% (GR^{50})[a].

Crop	Arsenic at GR^{50} (ppm)	
	Edible dry plant	Whole dry plant
Radish	76.0	43.8
Spinach	10.0	10.0
Green bean	4.2	3.7
Cabbage	1.5	3.4
Lima bean	1.0	1.7
Tomato	0.7	4.5

[a]Data obtained from crops grown immediately after sodium arsenate additions. (Modified from Woolson, 1973.)

Average values for As content in crops are shown in Table 7. The highest residues of As are found in plant roots (e.g. sugar beet and radish), with intermediate values in the vegetative top growth (e.g. spinach, grasses), and edible seeds and fruits containing the lowest levels of As (Liebig, 1966; Woolson, 1973; Walsh and Keeney, 1975). The limit set by the U.S. Public Health Service for arsenic content in fruits, crops and vegetables is 2.6 ppm (fresh weight). Most data are now presented in terms of dry matter, which does not facilitate comparison with this limit. It is possible that data given are affected by various contaminants which might account for the elevated levels quoted, e.g., potato peelings (Jacobs et al., 1970a) (Table 8) and radish (Woolson, 1973) (Table 6), where soil particles might be firmly adhered to the outer skin.

Table 7. Average As content of crops.

Crop	As Content (ppm, dry wt.)	Author
Sugar beet	2.83	Sandberg and Allen (1975)
Sorghum fodder	2.15	" " " "
Sorghum seed	0.17	" " " "
Cotton lint	1.27	" " " "
Cotton seed	0.06	" " " "
Bermuda grass	1.23	" " " "
Oats	0.80	" " " "
Sugar cane	0.30	Thoresby and Thornton (1979)
Alfalfa hay	0.29	" " "
Barley	0.13	" " "
Soybeans	0.12	" " "
Corn fodder	0.22	" " "
Corn seed	0.10	" " "
Wheat	0.07	" " "
Pasture	9.6	" " "
Lettuce	1.4	" " "
Strawberries	0.4	" " "
Barley grain	0.4	Schroeder and Balassa (1966)
Vegetables	0.26	" " "
Grain	0.70	" " "

Table 8.   Arsenic contents of crops after selected arsenical
            treatments.

Crop	Arsenic Content (ppm, dry wt.)		Treatment
	After 1 year	After 2 years	
Corn fodder	3.53	0.89	Sandberg and Allen (1975).
Corn seed	0.16	-	After treatments equiva-
Soybean seed	1.6	0.55	lent to 10 times the
Wheat	0.38	0.21	normal application of
			calcium arsenate
Cotton seed		5.2	
Soybean seed		4.5	
Sorghum		3.1	Johnson and Hiltbold
Corn grain		2.5	(1969). After normal
Crimson clover		1.9	methanearsonate treat-
Oats		1.7	ments
Vetch		1.6	
Potato peelings		84.0	
Potato tubers		0.5	Jacobs et al. (1970a).
Snap bean seeds		1.0	Treatments equivalent to
Peas		ND	arsenite treatment in one
Sweetcorn		ND	addition

ND = not detected.

Arsenic is a constituent of most plants, but little is known about its biochemical role. Several reports on the linear relationship between As content of vegetation and concentrations in soil of both total and soluble As suggest that plants take up As passively with the water flow. Some plants, particularly Douglas fir, show a remarkable ability to take up As far more than many of the associated plants. Such plants are useful guides to the recognition of subsurface mineralization with certain metals (Porter and Peterson, 1975; and Warren et al., 1968).

Thoresby and Thornton (1979) described the ready uptake of As by various plant species (Fig. 15). Apparently, As is translocated in plants since its concentration in the grain also has been reported. With increasing soil As, however, the highest As concentrations were always recorded in old leaves and in roots.
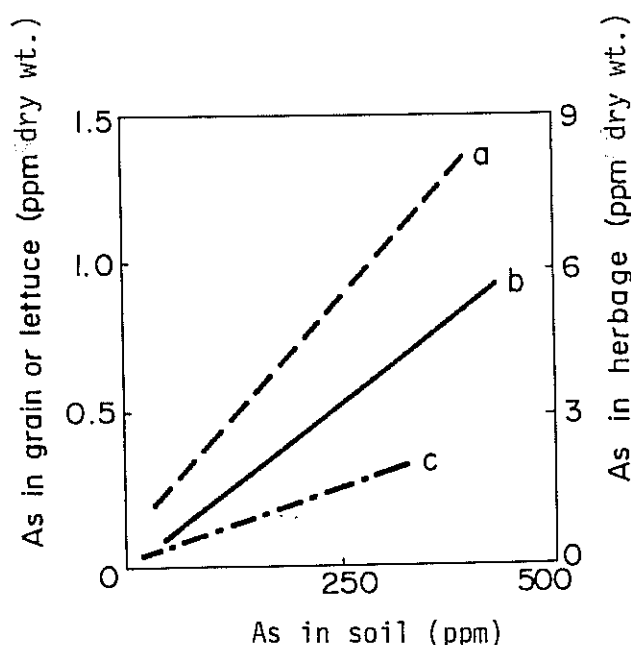
Fig. 15. Concentration of As in plants as a function of total
As. (a) Lettuce; (b) pasture herbage; (c) barley grains.
(Thoresby and Thornton, 1979)

Wallace et al. (1980) have shown that bush bean plants grown in solution culture with 10^{-4} M As (7.5 ppm As) accumulated approximately 4, 19, and 42 ppm As in leaves, stems, and roots, respectively, causing considerable damage. Decreased Mn, P, and Ca concentrations in all plant parts, and K in roots, were reported.

Gough et al. (1979) reviewed recent findings on As phytotoxicity and reported that the As content of injured leaves of fruit trees ranged from 2.1 to 8.2 ppm dry wt. In general, the residue tolerance for As in plants is established as 2 ppm dry wt. basis (Table 9). However, the critical value in rice plants is as high as 100 ppm dry wt. basis in tops and 1000 ppm dry wt. basis in roots (Kitagishi and Yamane, 1981). Davis et al. (1978) gave the critical value of 20 ppm dry wt. basis for barley seedlings.

Although there are some reports of the stimulating effects of As on the activity of soil microorganisms, As is known as a metabolic inhibitor, therefore, yield reduction of vegetation under a high level of bioavailable As should be expected. Apparently, As is less toxic when the plant is well supplied with P.

From updated work, Page et al. (In Preparation) observed that increases in Se uptake induced by As could not be attributed to what is considered the concentration effect due to yield decrease (Jarrell and Beverly, 1981). In other words, the observed increases in Se concentration in the alfalfa tissue are due to the synergistic effect of As

Table 9. Approximate concentrations of trace elements in mature leaf tissue generalized for various species (ppm dry wt.) (cited by Kabata-Pendias and Pendias, 1984, p. 57).

Element	Deficient, if less than the stated amounts of essential elements	Sufficient or normal	Excessive or toxic
Ag	-	0.5	5-10
As	-	1-1.7	5-20
B	5-30	10-200	50-200
Ba	-	-	500
Be	-	<1-7	10-50
Cd	-	0.05-0.2	5-30
Co	-	0.02-1	15-50
Cr	-	0.1-0.5	5-30
Cu	2-5	5-30	20-100
F	-	5-30	50-500
Hg	-	-	1-3
Li	-	3	5-50
Mn	15-25	20-300	300-500
Mo	0.1-0.3	0.2-1	10-50
Ni	-	0.1-5	10-100
Pb	-	5-10	30-300
Se	-	0.01-2	5-30
Sn	-	-	60
Sb	-	7-50	150
Ti	-	-	50-200
Tl	-	-	20
V	-	0.2-1.5	5-10
Zn	10-20	27-150	100-400
Zr	-	-	15

Note: Values are not given for very sensitive or highly tolerant plant species.

instead of the adverse effect of Se _per se_ on the yield of alfalfa. Connecting this phenomenon to the present situation of the west side, SJV, this synergistic effect of As, however, indicate that decreased Se concentration in the plant tissue could have resulted from decreased concentration of As in the irrigation waters.

Arsenic in Soils

The physical and chemical characteristics of soil affect its adsorptive capacities and therefore will affect the availability of As to plants. A wide variety of arsenicals can be absorbed by plants, but they have different toxic effects. The transformations occurring in the soil and the availability of the arsenicals are two important factors to be considered when studying the plant-soil system.

Bohn (1976) calculated that under the E_h and pH conditions likely to be encountered in soils, inorganic As could be present in solution as either arsenate or arsenite. Under reducing conditions, As-sulphur complex ions may be present and arsenite would be likely to be the dominant form (Deuel and Swoboda, 1972). Elemental As and arsine can also exist in strongly reducing environments (Walsh and Keeney, 1975). However, arsenate would be the stable oxidation state in oxygenated environments, with $H_2AsO_4^-$ predominating under acidic conditions and $HAsO_4^{2-}$ predominating under alkaline conditions.

In the last decade, experimental techniques have been developed to separate the inorganic and organic species of arsenic found in the environment (Braman and Foreback, 1973; Andreae, 1977). These have been utilized by some reserachers to investigate the arsenic species in the soils. Braman (1975) showed that dimethylarsinic acid (cacodylic acid) may be a ubiquitous arsenic compound found in all soils and predominant in many. Porter and Peterson (1977a,b), however, found that arsenate was the predominant water-soluble form in mine spoils, although dimethylarsinic compounds were occasionally detected. Woolson (1973) stated that regardless of the form in which the arsenical is applied, it is eventually oxidized and metabolized to arsenate. In later work, when more analytical techniques were available, he suggested that trimethylarsine (TMA) may also be an important compound (Woolson, 1977).

The relative proportions of ionic and molecular forms of organo-arsenicals are determined primarily by pH of the solution (Hiltbold, 1975). In most agricultural soils (pH 5.0-7.0) the univalent ion of methane-arsonates predominates, but both the cacodylate ion and acid may occur in these soils.

Little is known about the As compounds in soils, but their formation is good evidence that arsenate in soils behave like phosphate (Norrish, 1975; Woolson et al., 1973).

Several strains of bacteria accelerate the oxidation of arsenites to arsenates and are also involved in methylation and alkylation of As, thus microbiota may highly govern the processes of As migration, precipitation and volatilization (Boyle and Jonasson, 1973; Jernelov, 1975; Weinberg, 1977).

During studies of the persistence of inorganic and organic arsenicals the importance of microbial transformations has become apparent. Both oxidative and reductive changes in methanearsonates and cacodylic acid occur in soil (Hiltbold et al., 1974). Oxidation of the methyl carbon of disodium methanearsonic acid (DSMA) to carbon dioxide occurs under aerobic conditions and is directly affected by the amount of organic matter available for microbial activity (Dickens and Hiltbold, 1967).

Both iron and phosphate concentrations present in the systems were found to be significant factors in establishing the arsenic levels (Deuel and Swoboda, 1972; and Crecelins, 1975).

It has been suggested that As may substitute for phosphorus in DNA and produce genetic damage (Paton and Allison, 1972). Neurological abnormalities have been detected in a populace drinking arsenic contaminated waters at concentrations slightly greater than 0.1 mg/L (Grantham and Jones, 1978). The primary drinking water standard established by the U.S. Environmental Protection Agency recommends that public water supply sources should contain no more than 0.05 mg/L of arsenic in order to ensure a reasonable factor of safety in protecting the health of the population (U.S. Environmental Protection Agency, 1976).

Although our understanding of the mechanisms of As toxicity is far from complete at this time, there is evidence to suggest at least some of the biochemical effects in animals are derived from an effect of As or cellular respiration similar to that observed in vitro and in single cell organisms. Mitochondria appear to be the most sensitive organelle both ultrastructurally (Fowler et al., 1977, 1979; Fowler and Woods, 1979) and functionally in vivo exposed animal systems. Bertol'ero et al. (1981) have shown that 50-90% of the filterable As in a cell is present in the form of dimethylarsinic acid within 6 hours of exposure and that the non-filterable arsenic is bound to what appear to be high molecular weight proteins. These authors, however, suggest that the As bound to the proteins is in the inorganic form, although they do not specify whether it is bound as As(III) or As(V).

Kitagishi and Yamane (1981) have reviewed several studies on As behavior in contaminated soils and have shown that paddy soils accumulated most often considerable amounts of As and that fact is due to the high sorption capacity of these soils and also to the As transportation by irrigation water. Since As behavior is dependent on the soil oxidation state, this element varied in its vertical distribution. For example, in heavy gley soil As is accumulated only in the top horizon

and is readily leached from the surface layer with a high reduction potential. The As pattern in light, well-drained soils is almost the opposite (Fig. 16).
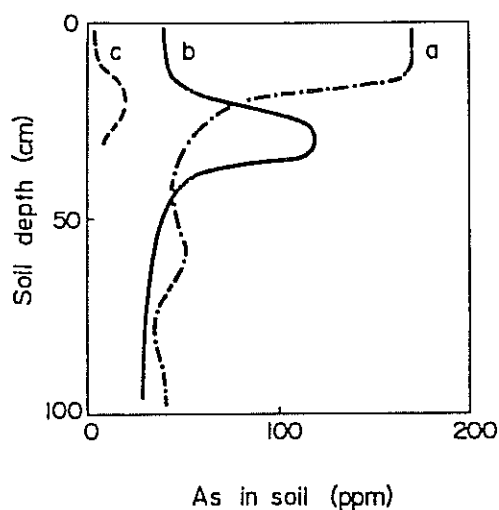

Fig. 16. Patterns of vertical distribution of total As in polluted soils from a nonferrous metal mining area in Japan. (a) Heavy gley soil; (b) light gley soil; (c) unpolluted paddy soil. (Kitagishi and Yamane, 1981)

The mobility of As in soil was shown to be proportional to the As added and inversely proportional to the As content of tissue and to Fe and Al contents. The toxicity of As depends on the concentration of soluble As, and plant growth response may also be related to total soil As (Fig. 17).
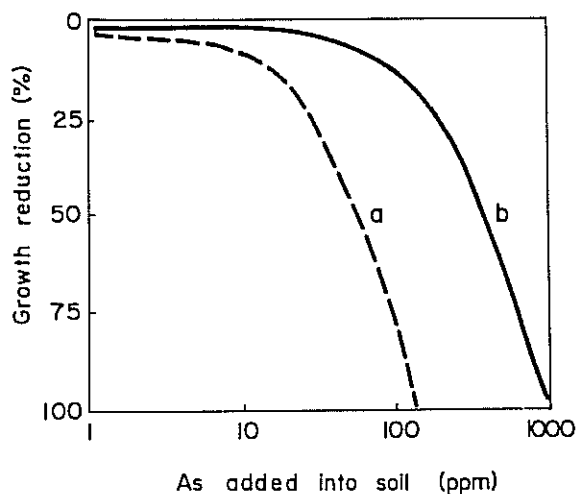

Fig. 17. Corn growth response to As added to two soils. (a) Light soil with low organic matter content and with kaolinitic clay predominating; (b) heavy soil with high organic matter content and with vermiculitic clay predominating.*

Phytotoxicity of As is highly dependent on soil properties. In heavy soil about 90% growth reduction appears at 1000 ppm As addition, whereas in light soil 100 ppm As is equally toxic (Woolson et al., 1973). The maximum allowable limit of As in paddy soils is proposed as 15 ppm (Kitagishi and Yamane, 1981).

The toxicity of As in soils may be overcome in several ways, depending on As pollution sources and on soil properties. Increasing the oxidation state of flooded (paddy) soils limits As bioavailability (Kitagishi and Yamane, 1981). Application of materials that produce precipitates with As in soil (e.g., less than 10 ppm of soluble As (in 0.05 N HCl) (Hanada et al., 1975). Also fertilizing, mainly the application of phosphate, decreases As bioavailability. However, the literature on the effect of phosphate on the retention of As in soils is confused, because phosphate could also displace adsorbed or fixed As from sorbing complexes and thereby initially increase the amount of soluble As in soils. The alleviating effect of S application on As toxicity has also been reported. Kitagishi and Yamane (1981) have reviewed this topic and presented several results that require further study.

Arsenic has been detected in southern Tulare County and northern Kern County, particularly in areas surrounding Allensworth and Delano where it occurs naturally in soils and ground water. In the southern area, some subsurface drain samples concentrations of As ranged from 0.01 mg/L to 1.00 mg/L (SJV Drainage Monitoring Program, 1986). These levels, however, tend to indicate a slight decrease in arsenic concentration with time. In 1984 for a concentration of 0.02 to 1.10 mg/L was reported throughout the southern area (SJV Drainage Monitoring Program, 1984). Six out of 22 samples analyzed for As in the southern area exceeded the drinking water guideline of 0.05 mg/L. In another area known to have high Se, Deverel et al. (1984) found As concentrations varying from <1 ug/L to 82 ug/L (with the median value of 2 ug/L).

Guideline

Arsenic accumulates in the soil in soluble, labile and residual forms. Only small concentrations are found in the soil solution so that leaching is extremely small. The general equation

$$\text{Soluble As} \rightleftharpoons \text{Labile As} \rightleftharpoons \text{Residual As}$$

can be used to illustrate reactions of As in soils. When soluble As is added there is a rapid conversion to the adsorbed or labile form and as the labile form increases there is a slow conversion to the highly stable insoluble residual form. In alkaline soils dominated by calcium the residual As most likely consists of insoluble calcium arsenates.

The added As accumulates in surface soils and with cultivation it gets mixed into the cultivated layer. Removal by plants is small in comparison to inputs when the As concentration in the irrigation water

approaches 100 ug/L and leaching is so small that it is not significant. Thus, the only sink for As is in its conversion to residual forms.

Once As has accumulated in soils to a level toxic to plants there is no fast method of resolving its toxicity which severely restricts the types of plants that can be grown. With time (years or decades) the slow reaction to residual forms will gradually reduce the severity of the toxicity.

Based on the review presented in this report, we have found no evidence supporting a change in the recommended maximum concentration of 100 ug As/L in irrigation waters (National Academy of Sciences, 1973). Assuming water is added at an annual rate of 10,000 m^3/ha this maximum concentration represents 1.0 kg/ha per year. Small removals in crops and by leaching and conversions to residual forms will prevent the accumulation to toxic levels for an indefinite period of time.

CHROMIUM

Introduction

The Cr content of acid igneous and sedimentary rocks is much lower than the average content of the earth's crust and commonly ranges from 5 to 120 ppm, being the highest in argillaceous sediments. Chromium shows highly variable oxidation states (from +2 to +6) and it is also known to form complex anionic and cationic ions, e.g., $Cr(OH)^{2+}$, CrO_4^2, CrO_3^{3-}. Naturally occurring Cr compounds have valences of +3 (chromic) and +6 (chromate). Highly oxidized forms of Cr are much less stable than Cr^{3+}.

In general, Cr^{3+} closely resembles Fe^{3+} and Al^{3+} in ionic size and in geochemical properties. However, under progressive oxidation Cr forms the chromate ion (CrO_4^{2-}), which is slightly mobile and also is easily sorbed by clays and hydrous oxides.

The behavior of soil Cr has been extensively studied by Bartlett and Kimble (1976), Bartlett and James (1979), Cary et al. (1977a), Bloomfield and Pruden (1980) and Grove and Ellis (1980). It has been shown that most of the soil Cr occurs at Cr^{3+} and is within the mineral structures or forms of mixed Cr^{3+} and Fe^{3+} oxides. Since Cr^{3+} is slightly mobile only in very acid media, and at pH 5.5 is almost completely precipitated, its compounds are considered to be very stable in soils. On the other hand, Cr^{6+} is very unstable in soils and is easily mobilized in both acid and alkaline soils (Fig. 18).
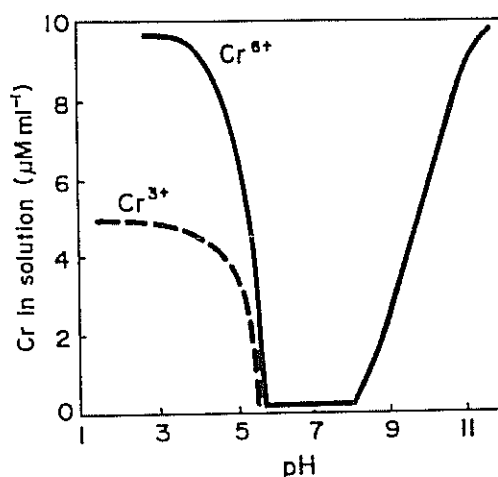

Fig. 18. Solubility of trivalent and hexavalent Cr as a function of pH. (Bartlett and Kimble, 1976)

El-Bassam et al. (1975) and Griffin et al. (1977) emphasized that Cr behavior is governed by both soil pH and redox-potential. The ready conversion of soluble Cr^{6+} to insoluble Cr^{3+} under normal soil conditions is of great importance because it is responsible for the low Cr availability to plants. Although the reduction of Cr^{6+} and Cr^{4+} is commonly reported, the oxidation of Cr^{3+} in soils has also been observed, apparently as an effect of the oxidizing ability of Mn compounds (Bartlet and James, 1979).

The immobility of soil Cr may be responsible for an inadequate Cr supply to plants. Chromium is of nutritional importance because it is a required element in human and animal nutrition. However, Cr added to soil appears to be very inefficient in terms of its recovery by food crops, although it causes an increase of this element in various plants (Cary et al., 1977). The Cr added to soils is usually accumulated at the thin top layer. El-Bassam et al. (1975) found that after 80 years of irrigation with sewage sludge containing 112 ppm Cr, the metal concentration in soil increased from 43 to 113 ppm. Chaney et al. (1981) extensively discussed the Cr hazard in biological waste management and stated that the food chain is well protected from an excess of Cr by the "soil-plant barrier". Chang et al. (1984) found over 90% of Cr in sewage sludge-treated soils (0, 22.5, 45, and 90 mg ha^{-1} y^{-1}) was found in the 0-15 cm soil depth, to which sludge was incorporated. Although crop absorption of heavy metals has increased with the sludge application rates, the total uptake amounted to <1% of the metal introduced through sludge application. Average metal recoveries from the soil ranged from approximately 35%. Liming, P application, and organic matter are known to be effective in reducing chromate toxicity in Cr-polluted soils. If contamination of soils is by Cr^{6+}, acidification and then reducing agents (e.g., S and leaf litter) could be used to speed the Cr^{6+} reduction. After the reduction, liming acid soils to increase the precipitation of Cr^{3+} compounds might be advisable (Grove and Ellis, 1980).

Soluble Chromium Concentrations

Major problems arise in determining chromium in natural waters due to its very low concentration. In addition to the need of a very sensitive method, contamination, sorption and species alteration can cause extremely large analytical errors.

Naturally occurring Cr concentrations in water arise from mineral weathering processes, soluble organic Cr, sediment load, and precipitation. Out of 170 lakes sampled in the high Sierra Nevada in California, only two contained as much as 5 ppb chromium. The pH of these lakes ranged from 4.7 to 7.3 with a mean and median value of 6.0 (Bradford et al., 1968). Robertson (1975) reported Cr(VI) present in ground water of the Paradise Valley, Arizona, at concentrations as high as 220 ppb. The pH of this water ranged from 7.8 to 9 with Eh values from 0.4 V to 2.5 V. In saline waters of Australia from 62% to 87% of the labile chromium present (<1 ppb) was Cr(VI) (Batley and Matousek, 1980).

Cr in SJV and the West Side

Data for Cr reported by Deverel et al. (1984) ranged from <1 to 170 ug/L and with the median value of 10 ug/L in surface drain water samples analyzed. Cr concentrations varied from 0.00 mg/L to 0.11 mg/L in the central area and from 0.00 mg/L to 0.02 mg/L in the southern area (SJV-Drainage Monitoring Program, 1986). These levels, however, are considered as rather low concentrations and therefore not hazardous because of soil accumulation and/or uptake by crops.

Plants

The Cr content of plants has received much attention since the relatively recent discovery that Cr participates in glucose and cholesterol metabolism, and therefore is essential to man and animals (Schroeder et al., 1962). There is not much literature on Cr in plants. Also, there is no evidence yet of an essential role of Cr in plant metabolism, although Mertz (1969) has reviewed the positive effects on plant growth of Cr applications to soils having a low soluble Cr content. The Cr content in plants is controlled mainly by the soluble Cr content of the soils. Most soils contain significant amounts of Cr, but its availability to plants is highly limited. However, the addition of Cr to soil affects the Cr content of plants, and the rate of Cr uptake by plants is dependent on several soil and plant factors. Usually a higher Cr content is observed in roots than in leaves or shoots, whereas the lowest concentration is in grains (Fig. 19).
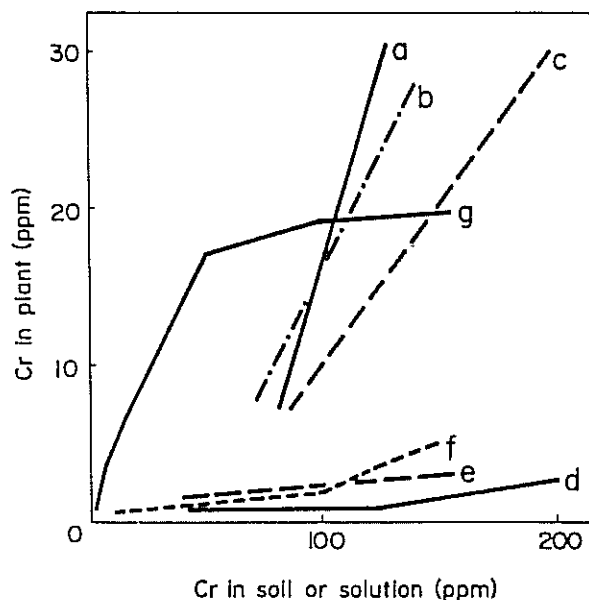

Fig. 19. Concentration of Cr in plant tissues as a function of Cr content of soil. (a) Potato stalks; (b) corn leaves; (c) wheat straw; (d) wheat grains; (e) barley grains; (f) tomato tops; (g) tomato roots. (Cary et al., 1977; and Diez and Rosopulo, 1976)

A low rate of Cr uptake by plants from the soluble fraction of this metal is related to the mechanism of uptake by roots. Apparently, root tissues are not capable of stimulating the reduction of Cr^{3+} to readily soluble Cr^{2+}, which is the key process in Fe absorption and translocation of Cr in plants seem to be similar to those of Fe, which is reflected in a fairly stable Cr/Fe ratio in plant tissues (Cary et al., 1977). Tiffin (1977) concluded that Cr is transported in plants as anionic complexes which have been identified in the extracts of plant tissues and in xylem fluid. Although stimulating effects of Cr on plants have been observed by several authors, the phytotoxicity of Cr has been often reported, especially in plants on soils developed from ultrabasic rocks. Anderson et al. (1973) reported toxicity in oats having a Cr content of 49 ppm (dry wt.) where grown on soil containing 634 ppm Cr. Turner and Rust (1971) observed initial symptoms of Cr toxicity with the addition of as little as 0.5 ppm Cr to the nutrient culture, and 60 ppm to the soil culture. These Cr additions resulted in decreased concentrations of almost all major nutrients in tops and K, P, Fe and Mg in roots. The antagonistic interaction between Cr and Mn, Cu, and B has also been reported by Turner and Rust (1971), and this can be related to interferences both within the soil medium and in the plant tissues. The toxicity of Cr depends on its oxidation stage, but is also related to readily available forms of chromate. The phytotoxic concentrations of Cr in tops of plants were reported as follows (dry wt. basis): 18 to 24 ppm in tobacco, 4 to 8 ppm in corn, 10 ppm in barley seedlings and 10 to 100 ppm in rice (Davis et al., 1978; Gough et al., 1979; and Kitagishi and Yamane, 1981).

Symptoms of Cr toxicity appear as wilting of tops and root injury; also chlorosis in young leaves. Chlorotic bands on cereals, and brownish-red leaves are typical features. Increased levels of Cr in the nutrient solution (up to 10^4 uM) are reported to disorganize the fine structure of chloroplasts and the chloroplast membranes of LEMNA MINOR (duckweed) (Baszynski et al., 1981).

Anthropogenic sources of Cr are responsible for the elevated content of this metal in plants. Czarnowska (1974) reported mean Cr concentrations in grass near city streets to be as high as 17 ppm (dry wt. basis). Kitagishi and Yamane (1981) gave the range in Cr in lichens collected within urban areas to be 5 to 10 ppm (dry wt. basis). Folkeson (1979) found 5 ppm Cr (dry wt. basis) in mosses near peat-fired plants and 9 ppm Cr in mosses from the edge of a waste heap of the ash, as contrasted with background concentrations of 1 to 1.5 ppm. Gough and Severson (1976) found 500 ppm Cr in ash of sagebrush from the vicinity of a P fertilizer factory.

Wastes containing increased Cr concentrations are reported by Chaney et al. (1981) not to be hazardous to human health; however, there is evidence of Cr toxicity to livestock grazing grass with an elevated Cr content due to rich sewage sludge amendment (Kabata Pendias and Pendias, 1979). Sykes et al. (1981) reported that their results fully confirmed the nontoxicity of Cr III, at least at a level of 500 mg/kg in

the soil.   The concentration of Cr III in the soil had a negligible effect on the uptake of Cr III by the edible portions of the crops.

McGrath (1982) stated that tri- and hexa-valent chromium were both absorbed by oat and were equally toxic when supplied at 2 to 200 uM in nutrient solution. The proportion of Cr translocated to the shoots was similar, regardless of the form supplied to roots. Problems of Cr toxicity have been reported under conditions of high Cr(VI) availability or at low pH where sufficient soluble Cr(III) is present. At higher pH values, as with aluminum, precipitation of the Cr(III) hydroxides makes the metal ion unavailable to plants. The effects of Cr(VI) and Cr(III) ions appear to be very different, but their effect on proton extrusion might explain their toxicity on plants as well as the stimulative effect at very low concentration (Pratt, 1966). Cr(VI) ions inhibit the capability of root tissue to acidify the incubation medium and to absorb K^+ ions (Zaccheo et al., 1982).

Guideline

The critical chemistry of Cr in respect to plant accumulation from the environment revolves around the reduction of Cr(VI) to Cr(III), the oxidation of Cr(III) to Cr(VI), and the relative stability of Cr(III) compounds once formed.   Elemental and inorganic trivalent chromium appear to offer little reason for concern as plant toxicant.   These species are relatively unavailable to plants.   One can speculate that the same is true of many organic chromium compounds. Chromium (III) may be toxic to some plants at a solution concentration of 5 ppm (Pratt, 1966).   Generally, solution chromium concentrations would not reach 5 ppm except in sandy soils or near the source of pollution. Hexavalent chromium is water soluble and a strong oxidant. Therefore, its environmental effects will be greatest. It can remain as Cr(VI) in some soils for a relatively long time, especially in those that are basic or have low organic matter contents. Chromium VI is generally considered to be more toxic than Cr(III) (Cary, 1982).

Although stimulating effects of Cr on plants have been observed by several authors, the phytotoxicity of Cr in plants has often been reported.   However, problems of Cr toxicity have been reported under conditions of high Cr(VI) availability or at low pH where sufficient soluble Cr(III) is present (McGrath, 1982). Furthermore, at higher pH values (as the case of the southern area, SJV), precipitation of the Cr(III) hydroxides makes the metal ion unavailable to plants.   Data reported from the present study area, i.e., southern SJV, indicate that the chromium concentrations varied from <1 to 170 ug/L (with the median value of 10 ug/L) in surface drain water samples analyzed (Deverel et al., 1984).   Thus, from the presented data, we find no reason or evidence for changing the existing guideline for Cr (0.1 mg/L, National Academy of Sciences, 1973) concentration in the irrigation water in general, and for the west side of the SJV in particular.

FLUORIDE (F)

The behavior of F in soils has been studied by Larsen and Widdowson (1971), Perrott et al. (1976), Chhabra et al., (1980), and Omueti and Jones (1980). The results obtained show that the mobility of F in soils is complex and that the predominant factors controlling the level of this ion in the soil solution are the amount of clay minerals, the soil pH, and the concentrations of Ca and P in soils. In general, the greatest adsorption of F by soil mineral components is either at the distinct acid range of pH, or at about pH 6 to 7 (Fig. 20).
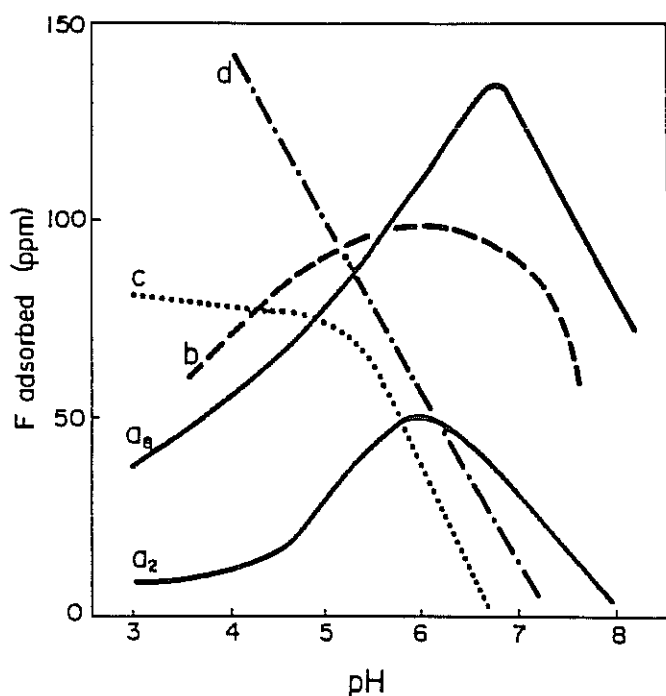
Fig. 20. Adsorption of F by soil and clay as a function of the pH. (a_2 and a_4) Soil equilibrated against 2 and 8 mg F$^-$ per 1·ℓ solution. respectively; (b) bentonite; (c) bauxite; (d) kaolinite. All clays equilibrated against 2 mg F$^-$ per 1·ℓ solution. (Omueti and Jones, 1977)

Fluoroapatite is considered to be the most common form of F in soils. However, several fluorides (e.g., CaF, AlF$_3$) and aluminosilicates (e.g., Al$_2$(SiF$_6$)$_2$) are also reported to occur in soils. Flouride is also known to form complex ions with Al (AlF^{2+}, AlF$_2^+$, AlF$_4^-$). Therefore, the mobile F$^-$ in the soil solution might control the activity of Al^{3+} in soils (Lindsay, 1979).

Under natural soil conditions F is slightly mobile, but it is not accumulated in the surface horizon, especially of acid soils. The high solubility of F in acid soils is attributed to the occurrence of readily soluble fluorides such as NaF, KF, NH_4F, whereas AlF_3 is known to be of low solubility. Thus, the increasing F content with depth reflects the response to the soil pH; however, the increased clay content with increased depth usually contributes more to the F distribution in soil profiles. This relationship with clay content has been reported by Piotrowska and Wiacek (1975) and Omueti and Jones (1980).

In calcareous soils the formation of slightly soluble CaF_2 and F complexes with Fe, Al, and Si are responsible for the low migration of this element. In sodic soils, on the other hand, a high exchangeable Na affects increased solubility of F. The F concentration in soil is inherited from parent material, whereas its distribution in soil profiles is a function of soil-forming processes, of which the degree of weathering and clay content are the most pronounced. Apparently, F has been lost from the surface horizons of most soils (Fig. 21) and this partly reflects a low F affinity for organic matter. Omueti and Jones (1980) gave the range in F concentrations in organic matter of surface horizons to be as low as 0.03 to 0.12 ppm.
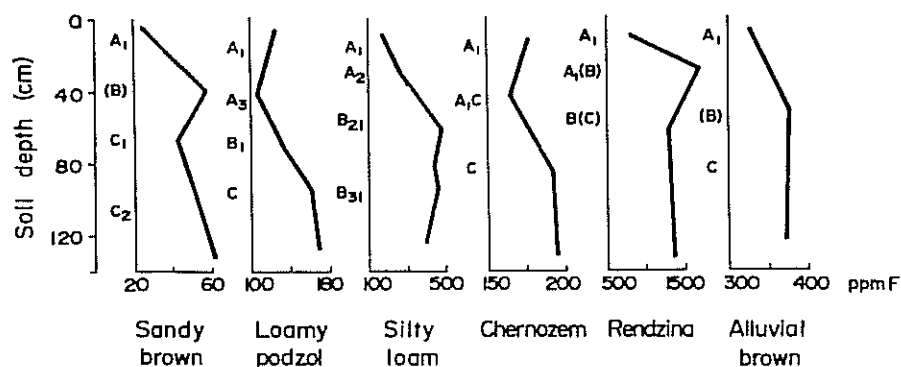

Fig. 21. Distribution of F in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

Most of the F added to soil is either effectively fixed by soil components (clays, Ca, and P) or readily leached from light soils (Davies, 1980; Weinstein, 1977).

The most important hazard of F contamination in soils concerns changes in soil properties due to the great chemical activity of hydrofluoric acid which is temporarily formed from both solid and gaseous F pollutants. Bolewski et al. (1976) reported the destruction of humic mineral complexes resulting in a significant loss of organic matter in soils. Thus, the availability of F in a polluted soil is a function of a number of soil characteristics and is not the only cause of limited plant growth on those soils (Russel and Swiecicki, 1978).

In general, fluoride content beyond 10 ppm in irrigation water is considered harmful for plant growth, while more than 1 ppm fluoride in drinking waters is questionable for drinking purposes (Singh and Narain, 1980). Paliwal et al. (1969) reported that irrigation water having fluoride concentrations more than 7 ppm is detrimental for wheat. Brean and Weinstein (1985) stated that the soil F content is not an important source of F to plants and therefore to herbivores in the area. This is probably because the fluoride ion has limited solubility in soil water (Larsen and Widdowson, 1971), therefore, it is not surprising that uptake is relatively low and that there is little or no relationship between uptake and total or water-soluble fluoride (Cooke et al., 1976).

Plant Absorption and Translocation

The availability of F to plants usually is not related closely to the total or soluble F content of a soil. However, under certain soil and plant conditions the F content of plants seems to reflect its occurrence in soil (Shupe and Sharma, 1976). Bieliyakova (1977) gave the ratio of F in plant ash to F in topsoil as 0.2 and 0.6 for culti- vated and natural vegetation, respectively. These values indicate a relatively low F bioavailability.

The soluble F fraction in soil is taken up passively by roots and apparently is easily transported in plants. This statement is supported by the observation of a ready F uptake from fields irrigated with F-containing waters.

Van Der Putte (personal communication) found that F absorption from the solution media by alfalfa and wheat is positively correlated with F concentration in the media. He obtained results that indicated a very high accumulation in the grains (up to 3250 ppm dry wt. basis at 50 ppm F^- in solution). This phenomenon reflected a possible influence of the formation of an F complex that may be more easily taken up by plants than are F ions.

Although it has been shown that plants can take up F quite easily from polluted soils, the bioavailability of soil F is of much less significance than that from airborne compounds. The effects of atmo- spheric F depositions, both in soils and plant surfaces have been extensively studied. The results, as summarized by Groth (1975) and Weinstein (1977), have indicated that the deposition of airborne F on

soil has little or no effect on the F content of plants, but this conclusion is not a unanimous one.

Conclusions

Under natural soil conditions F is slightly mobile, but it is not accumulated in the surface horizon. In calcareous soils the formation of slightly soluble CaF_2 and F complexes with Fe, Al, and Si are responsible for the low migration of this element.

The F compounds added to soils by irrigation are usually readily soluble and thus available to plants. But some of the added F to soil is fixed by soil components (clays, Ca, and P). Nevertheless, easily soluble F-bearing fertilizers (e.g., potassium fluoroborate) or sewage sludges may effect a remarkable increase in the bioaccumulation of F from soils (Davies, 1980; Weinstein, 1977).

The existing guideline, 1 mg/L, as maximum recommended concentration in irrigation waters (National Academy of Sciences, 1973) was based on reported work mainly of MacIntire et al. (1942, 1948, 1951, 1955a, 1955b) suggesting that 360 pounds of F per acre on acid sandy soils can produce phytotoxicities and that in neutral sandy soils toxicities can be expected as rates of 720 pounds/acre. In fine textured neutral and alkaline soils (such as the west side - SJV soils) the capacity of soils to inactivate fluoride is relatively high.

Following these conditions, the present guideline as 1 mg L^{-1} may appear as rather conservative, while the updated review presented here illustrated a wide range of F toxic limits in the irrigation water. Kumar (1981) reported that 5 ppm F was inhibitory to germination of rice and the difference is apparently clear even at 0.5 ppm. Paliwal (1969) stated that having more than 7 ppm is detrimental for wheat and Singh and Marian (1980) reported that beyond 10 ppm F is considered harmful for plant growth. Also the solubility of F in soils is highly variable, tends to be higher at pH below 5 and above 6 (Larsen and Widdowson, 1971) and further work is needed to characterize the chemical nature of both fractions in the soil and how they relate to the absorption of F by plant roots.

In conclusion, due to the lack of information related to the unique conditions of the SJV, the existing guideline (1 mg L^{-1}), therefore, seems justified.

ALUMINUM

As one of the main constituents of the earth's crust, Al in rocks commonly ranged from 0.45 to 10%, and in shales (as in the SJV) from 7.8 to 8.8% (Kabata-Pendias and Pendias, 1984). The only stable and frequently occurring ion, Al^{3+}, is known to coordinate with oxygen-bearing ligands. In general, the solubility of Al hydroxides is low, especially at the pH range of 5 to 8, and solubility decreases with aging.

Aluminum toxicity is an important limiting factor for plant growth in many acid soils (Foy, 1974; Kamprath and Foy, 1971). The problem is particularly serious in strongly acid subsurface soil layers (below pH 5.5) that are difficult to lime. At pH values from about 5.5 to 8.0, soils have great capacities to precipitate soluble aluminum and to eliminate its toxicity. The reaction is dominantly a precipitation of Al-hydroxide. By the use of agricultural limestone to maintain the pH at about 5.5 or above, Al toxicities are highly improbable. Most irrigated soils (such as the west side of the SJV) are naturally alkaline and many are highly buffered with calcium carbonate. In these situations Al toxicity is effectively prevented.

With only a few exceptions, as soils become more acid (pH < 5.5) exchangeable and soluble aluminum develop by dissolution of oxides and hydroxides or by decomposition of clay minerals. Thus, without the introduction of aluminum, a toxicity of this element may develop and agriculture limestone must be added to keep the soil productive.

In nutrient solutions, toxicities are reported for a number of plants at aluminum concentrations of 1 mg/L (Pratt, 1966), whereas wheat is reported to show growth reduction at 0.1 mg/1 (Barnette, 1923). Liebig et al. (1942) found growth depressions of orange seedlings at 0.1 mg/L. Ligon and Pierre (1932) showed growth reduction of 60, 22, and 13 percent respectively for barley, corn, and sorghum at 1 mg/L. The extrapolation of these data to soil conditions is questionable but they do indicate the potential problem with soluble aluminum in irrigation waters. If management were not well developed for eliminating aluminum toxicity, a suggested maximum concentration of about 0.05 mg/1 would need to be made to insure that the aluminum added in waters would not contribute to aluminum toxicity in highly acid soils.

In spite of the potential toxicity of aluminum, this is not the basis for the establishment of maximum concentrations in irrigation waters because ground limestone can be added where needed to control aluminum solubility in soils. Nevertheless, two disadvantages remain. One is that the salts that are the sources of soluble aluminum in waters will acidify the soil and contribute to the requirement for ground limestone to prevent the accumulation or development of soluble aluminum. This will be a disadvantage only in acid soils and will not be a problem in alkaline calcareous soils. The other disadvantage

will be a greater fixation of phosphate fertilizer by freshly precipi-
tated aluminum hydroxides.

In view of these disadvantages the existing guideline as maximum
concentration of aluminum is 5 mg/l (National Academy of Sciences,
1973). At rates of three acre-feet of water per acre per year the
calcium carbonate equivalent of the 5 mg/l concentration used for
100 years would be 11.5 tons per acre. In most irrigated soils, for
example, as in the west side of the SJV, this amount of limestone would
not have to be added because the soils have sufficient buffer capacity
to neutralize the aluminum salts, but in acid soils that require lime-
stone, the aluminum added in the water would contribute to the lime
requirement.

The total Al content of soils is inherited from parent rocks;
however, only that fraction of Al which is easily mobile and exchange-
able plays an important role in soil fertility (McLean, 1976). The
solutions of neutral soils contain Al in the order of about 400 ug L^{-1},
while in the soil solution at pH 4.4, Al concentration was reported to
be 5700 ug L^{-1} (Gough et al., 1979).

Aluminum is a common constituent of all plants and is reported to
occur in higher plants in order of about 200 ppm (dry weight). However,
the content of this element in plants varies greatly, depending on soil
and plant factors (Table 10).

The physiological function of Al in plants is not clear, although
there is some evidence that low levels of Al can have a beneficial
effect on plant growth, especially in Al-tolerant plant species (Clark,
1977; Foy et al., 1978). Aluminum injury or toxicity is often reported
for plants grown in acid soils. Several recent reviews have been
published on this subject which emphasized that a high availability of
Al in acid soils is one of the limiting factors in the production of
most field crops (Baker, 1976; Foy et al., 1978; Reid, 1976).

In addition, in the leguminous plants, the development and function-
ing of the symbiosis with Rhizobium can be affected. For instance,
Ayanaba et al. (1982), Date and Halliday (1979), Dobereiner (1966),
Graham and Parker (1964), Graham et al. (1982), Keyser and Munns (1979a,
1979b), Munns et al. (1979), Lie (1969), Mayz and Manzi et al. (1983),
Vincent (1965, 1974) have demonstrated the harmful effect of low pH and
of Al and Mn toxicity on the survival and multiplication of Rhizobium in
soil or artificial media. Also, a reduction in nodule number in both
temperate and tropical species has been observed (Andrew, 1976; Carvalho
et al., 1981, 1982; Graham et al., 1982; Keyser et al., 1979; Lie, 1969;
Loneragan and Dowling, 1958; Lowther and Loneragan, 1970; Munns et al.,
1979; Small, 1968) as well as an inhibition of infection (Lie, 1969;
Lowther and Loneragan, 1970), curling of root hairs (Munns, 1968) and
nitrogenese activity (Munns, 1978; Munns et al., 1979).

Table 10. Aluminum content of food and forage plants (ppm)

Plant	Tissue sample	Fresh wt.(a) basis	Dry wt. basis
Barley	Grains	–	135(b), 10(c)
Oats	Grains	–	82(b)
Sweet corn	Grains	–	2.6
Cabbage	Leaves	1.5	8.8
Spinach	Leaves	–	104(d)
Lettuce	Leaves	0.1	73
Carrot	Roots	0.4	7.8
Onion	Bulbs	–	63
Potato	Tubers	3.8	76(d), 13
Tomato	Fruits	–	20
Apple	Fruits	0.9	7.2
Orange	Fruits	1.4	15
Legumes	Tops	–	85-3,470(e)
Grass, timothy	Tops	–	6.5-23.5(f)
Grasses*	Tops	–	60-14,500(g)
Grasses	Tops	–	50-3,410(e)

Note: Sources are as follows: Shacklette, 1980; a, Montford et al., 1980; b, Burton, 1979; c, Liu et al., 1974; d, Metson et al., 1979; e, Baumeister and Ernst, 1978; f, Paasikallio, 1978; g, Allen and Robinson, 1980.

*Sample from grass tetany pasture.

Guideline

A specific guideline for the Al concentrations in irrigation waters of the West Side of the SJV is not needed. The Al concentration is effectively controlled by the soil at levels that produce no adverse effects. The previous recommendation that irrigation waters contain no more than 5 mg/L (National Academy of Sciences, 1973) is probably more than adequate protection for all of irrigated agriculture.

LITHIUM

The common characteristic of the alkali trace elements (Li, Rb and Cs) is the single electron in the outermost energy level, resulting in highly reactive chemical behavior. The relative bonding force holding these monovalent cations is presented most often in the order $Cs^+ > Rb^+ > Li^+$. These cations do not usually form complex ionic species.

Soils

Lithium contents of soils are controlled more by conditions of soil formation than by their initial contents in parent rocks. The Li distribution in soil profiles follows the general trends of soil solution circulation; however, it may be highly irregular (Wells and Whitton, 1972).

The abundance of Li in surface soils, as presented in Tables 11 and 12 is fairly uniform in various soil units. The mean values for Li vary from 1.2 ppm in light organic soils to 98 ppm in alluvial soils. Lower contents of Li are reported for light sandy soils, especially those derived from glacial drift in a humid climate. In the arid climatic zones Li follows the upward movement of the soil solution and may precipitate at top horizons along with easily soluble salts of chlorides, sulfates, and borates. These reactions explain a relatively higher Li content of soils such as solonchaks, kastanozems, and prairie soils. Also intrazonal young soils derived from alluvium reveal elevated Li concentrations.

In the initial processes of soil formation, Li seems to be highly mobile, while later it may become more stable due to its firm bonding with clay minerals (Wells and Whitton, 1972). However, as Shakuri (1976) reported, water-soluble forms of Li in the soil profile reach up to about 5% of the total soil content and therefore Li is likely to occur in ground waters of areas having elevated Li contents in rocks and soils. Exchangeable soil Li is reported to be strongly associated with Ca and Mg (Davey and Wheeler, 1980).

Plants

Lithium is not known to be an essential plant nutrient, but there is some evidence that Li can affect plant growth and development (Angino et al., 1974).

Increased Li concentrations in soil is toxic to some plant species. Citrus trees are known to be the most susceptible to injury by an excess of Li, which is reported to be toxic at a concentration in leaves of 140 to 220 ppm. Threshold concentrations of Li in plants are highly variable, and moderate to severe toxic effects of 4 to 40 ppm Li concentration in citrus leaves (dry wt. basis) have been observed (Gough et

Table 11. Lithium content of surface soils of the U.S. (ppm dry wt.)
(Schacklette and Boerngen, 1984)

Soil	Range	Mean
Sandy soils and lithosols on sandstones	<5-50	16.5
Light loamy soils	9-46	24.5
Loess and soils on silt deposits	9-30	20.5
Clay and clay-loamy soils	10-64	23.5
Alluvial soils	10-120	34.0
Soils over granites and gneisses	10-45	23.5
Soils over volcanic rocks	15-41	25.5
Soils over limestones and calcareous rocks	6-88	26.5
Soils on Glacial till and drift	10-30	18.0
Light desert soils	9-69	25.0
Silty prairie soils	10-34	20.5
Chernozems and dark prairie soils	8-40	22.5
Organic light soils	<5-71	13.0
Forest soils	10-57	24.0
Various soils	<5-100	28.0

Table 12. Lithium content of surface soils of different countries (ppm dry wt.)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soil	U.S.S.R.	17-60	34	Borovik-Ramanova and Bielova,
	New Zealand	5-72	31	1974; Wells and Whitton, 1972
Loess and silty soils	New Zealand	-	95	Wells and Whitton, 1972
Loamy and clay. soils	New Zealand	1.4-130	45.5	Wells and Whitton, 1972
Soils on glacial till	Denmark	-	6.2	Tjell and Hovmand, 1972
Fluvisols	New Zealand	65-160	98	Tjell and Hovmand, 1972
Gleysols	New Zealand	50-100	68	Tjell and Hovmand, 1972
Rendzinas	U.S.S.R.	-	42	Aidiniyan, 1959
Kastanozems and brown soils	U.S.S.R.	31-48	37	Aidiniyan, 1959; Borovik-Ramanova; and Bielova, 1974
Ferralsols	U.S.S.R.	10-25	17	Borovik-Ramanova and Bielova, 1974
Solonchaks and solonetz	U.S.S.R	23-53	42	Borovik-Ramanova and Bielova,
	New Zealand	36-68	55	1974; Wells and Whitton, 1972
Chernozems	U.S.S.R.	20-65	45	Aidiniyan, 1959; Borovik-Ramanova and Bielova, 1974; and Shakuri, 1976
Prairie and meadow soils	U.S.S.R.	-	73	Shakuri, 1976
Histosols and other organic soil	Denmark	0.5-3.2	1.6	Tjell and Hovmand, 1972;
	New Zealand	0.01-2.8	1.2	Wells and Whitton, 1972
	New Zealand	0.01-2.8	1.2	Wells and Whitton, 1972
Forest soils	U.S.S.R.	25-65	50	Aidiniyan, 1959; Borovik-Ramanova and Bielova, 1974; Shakuri, 1976
Various soils	Denmark	-	8.6	Tjell and Hovmand, 1972
	New Zealand	10-100	64	Wells and Whitton, 1972
	Great Britain	-	25	Ure and Bacon, 1978
	38New Guinea	6-28	15	Davey and Wheeler, 1980

al., 1979). In high-Li soils damage to root tips of corn as well as necrotic spots in the interveinal leaf tissues and other nonspecific injury symptoms have been observed (Angino et al., 1974).

Calcium inhibits Li uptake by plants, therefore the addition of Ca salts to high-Li soil may reduce toxic effects of this element. Lithium is also toxic to many microorganisms, although the fungi Penicillium and Aspergillus adapt easily to higher Li concentrations in their growth media.

Plants of the Rosaceae family considered with the highest mean Li content (Table 4) have an index of 0.6, while for plants of the Polygonaceae have an index of 0.04. The highest value of this index, 0.8, however, was calculated for plants of the Solanaceae, members of which are known to have the highest tolerance to Li. Some plants of this family when grown in an aridic climatic zone accumulate more than 1000 ppm Li (Sievers and Cannon, 1973).

Table 13. Lithium content of plant families (ppm dry wt.)

Family	U.S.S.R.(a) (mean)	U.S.(b) (range)	New Zealand(c) (range)
Rosaceae	2.9	-	-
Ranunculaceae	2.0	-	-
Solanaceae	1.9	0.01-31 (1120(d)	-
Violaceae	1.3	0.01-3.1	<0.03-143
Leguminosae	0.67	-	-
Compositae	0.55	-	-
Cruciferae	0.54	-	-
Chenopodiaceae	0.32	-	-
Urticaceae	0.24	0.07-1.5	<0.01-13
Polygonaceae	0.10	-	-
Lichenes	-	0.02-0.3(e)	-

Note: Sources are as follows: a, Borovik-Romanova and Bielova, 1974; b, Angino et al., 1974; c, Wells and Whitton, 1972; d, Sievers and Cannon, 1973; e. Bowen, 1979.

Lithium appears to share the K^+ transport carrier and therefore is easily transported in plants, being located mainly in leaf tissues. The Li content of edible plant parts presented in Table 14 shows that some leaves accumulated a higher proportion of Li than did storage roots or bulbs. However, a higher Li content is very often reported for roots. The ratio of root to top for Li in ryegrass was 4.4, while for white clover it was 20 (Wells and Whitton, 1972). This may suggest that a

difference in plant tolerance to Li concentration is related mainly to mechanisms of biological transport barriers in root tissues.

Table 14. Lithium content of plant foodstuffs

Plant	Tissue sample	Dry wt. basis	Fresh wt. basis
Celery(a)	Leaves	6.6(a)	-
Chard(a)	Leaves	6.2(a)	-
Corn(a)	Ears and stover	0.8(a)	-
Corn(b)	Grains	0.05(b)	-
Cabbage	Leaves	0.5	4.9
Carrot	Roots	0.2	2.3
Lettuce	Leaves	0.3	2.0
Onion	Bulbs	0.06	1.6
Potato	Tubers	-	<4
Tomato	Fruits	-	<4
Apple	Fruits	-	<4
Orange	Fruits	0.2	5.3

Note: Sources are as follows: Shacklette, 1980;
a, Chapman, 1972; b, Duke, 1970

Wallace et al. (1977c) reported that, in most experimental treatments, bush beans accumulated more Li in shoots than in roots while growing in a solution culture with high concentrations of Li. They reported also that higher levels of Li decreased the Zn content in leaves and increased Ca, Fe, and Mn content in all plant tissues.

Guideline

The existing guidelines for Li, as minimum concentrations was based on its phytotoxicity, are 2.5 mg/L for continuous use on all soils except for citrus where the recommended maximum concentration is 0.075 mg/L. However, the supportive information used for this guideline showed that most crops can tolerate Li in nutrient solutions at concentrations up to 5 mg/L (Bingham et al., 1964; Bollard and Butler, 1966; Oertli, 1962). While Aldrich et al. (1951), Bradford (1963), and Hilgeman et al. (1970) have shown that citrus is more sensitive, and found that grapefruit developed severe symptoms of Li toxicity when irrigated with waters containing Li at 0.18 to 0.25 mg/L. Bradford (1963) reported that experience in California indicated slight toxicity of Li to citrus at 0.06 to 0.10 mg/L in the water.

From more recent work, Reharb and Wallace (1978) reported that the amount of Li necessary to cause yield reduction in cotton (Gossypium spp.) when grown in soil (about 1900 ug Li/g leaf material) was not

reached in solution cultures at 0.7 mg/L Li. A level of 7 mg/L Li in soil produced yield reductions in other species (Wallace et al., 1977c) of cotton. Wallihan et al. (1978) reported that threshold leaf concentration above which toxicity was evident is estimated at 80 ppm Li for tropic tomato plants grown in solution culture. Sneva (1979) showed that Li concentrations greater than 5 ppm depress the growth of roots and shoots of 3 cool season grasses. Gupta (1974) reported that growth of wheat and barley seedlings was not affected by levels of Li up to 5 ppm, but root growth was reduced at 10 ppm.

Data reported by Deverel et al. (1984) on shallow groundwater from the study area indicated that Li was not considered among the eight priority pollutants (U.S. EPA, 1979) and it did not occur in concentrations that approach or exceed the maximum concentrations specified by water quality criteria for freshwater aquatic life (U.S. Environmental Protection Agency, 1980). The level of Li found by Deverel et al. (1984) was far below the present level recommended here. The range of Li values reported by Deverel et al. (1984) was from 14 to 430 ug/L (with the median value of 90 ug/L).

In conclusion, the previous recommendations (National Academy of Sciences, 1973) that irrigation waters contain no more than 2.5 mg Li/L for general crops and no more than 0.075 mg/L for citrus appear to be appropriate for the west side of the SJV.

NICKEL

The Ni status in soils is highly dependent on the Ni content of parent rocks. However, the concentration of Ni in surface soils also reflects soil-forming processes and pollution. Soils throughout the world contain Ni within the broad range of from 1 to around 100 ppm, while the range for soils of the U.S. is from <5 to 200 ppm (Kubota, 1968; Shacklette and Boerngen, 1984). The highest Ni contents are always in clay and loamy soils, in soils over basic and volcanic rocks, and in organic-rich soils. Especially peaty serpentine soils are known for high Ni levels existing in easily soluble organic complexes (Nielsen et al., 1977). Also soils of arid and semiarid regions are likely to have high Ni contents. The mean value for world soils is calculated to be 20 ppm, and 19 ppm was reported for U.S. soils.

Nickel recently has become a serious pollutant that is released in the emissions from metal processing operations and from the increasing combustion of coal and oil. The application of sewage sludges and certain phosphate fertilizers may be important sources of Ni. In particular, Ni in sewage sludge that is present mainly in organic chelated forms is readily available to plants and therefore may be highly phytotoxic. Soil treatment, such as additions of lime, phosphate, or organic matter, are known to decrease Ni availability to plants.

As with the other trace elements, Ni in the solid phase of soils occurs in several chemical forms in the aqueous phase (i.e., soil solution). Nickel may occur in the ionic form and in complexes with either organic or inorganic ligands.

Plants

There is no evidence of an essential role of Ni in plant metabolism, although the reported beneficial effects of Ni on plant growth have stimulated speculation that this metal may have some essential function in plants (Mengel and Kirkby, 1978; Mishra and Kar, 1974).

Welch (1979) discussed recent reports that Ni is an essential component of the enzyme urease, and thus Ni may be required by nodulated legumes that transport N from roots to tops in forms of ureide compounds. Studies of the uptake and chemical behavior of Ni in plants are related mainly to its toxicity having possible implications with respect to animals and man. Although the transport and storage of Ni seems to be metabolically controlled, this metal is mobile in plants and is likely to be accumulated in both leaves and seeds (Diez and Rosopulo, 1976; Halstead et al., 1969; Welch and Cary, 1975).

Nickel is readily and rapidly taken up by plants from soils, and until certain Ni concentrations in plant tissues are reached, the adsorption is positively correlated with the soil Ni concentrations

(Fig. 22). Both plant and pedological factors affect the Ni uptake by plants, but the most pronounced factor is the influence of the soil pH. As Berrow and Burridge (1979) found, increasing the soil pH from 4.5 to 6.5 decreased the Ni content of oats grain by a factor of about 8 (Fig. 22).
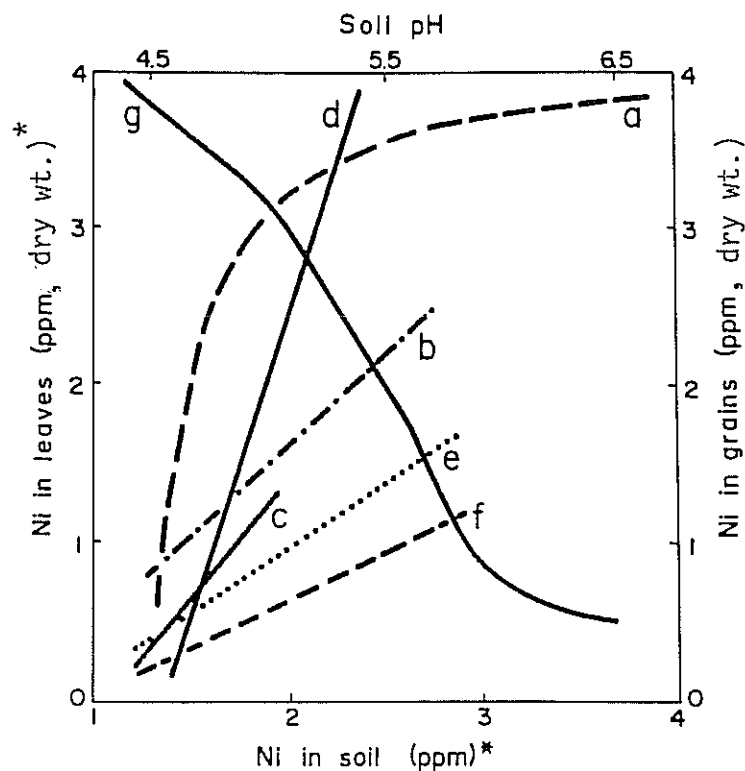

FIGURE 22. Ni concentrations in plants as a function of Ni content of soils. (a) leaves of *Alyssum* sp., accumulating Ni; (b) leaves of *A. montanum*, nonaccumulating Ni; (c) wheat leaves; (d) barley grains; (e) carrot roots; (f) radish roots. The influence of soil pH on Ni concentration in (g) oat grains. *Ni concentrations in soils, leaves and roots are given in powers of ten. (Berrow and Burridge, 1979).

The mechanism of Ni toxicity to plants is not well understood, although the restricted growth of plants and injuries caused by an excess of this metal have been observed for quite a long time. The most common symptom of Ni phytotoxicity is chlorosis, which seems to be an induced Fe chlorosis. Indeed, Foy et al. (1978) reported a low foliar Fe level at toxic concentrations of Ni in the growth medium. With plants under Ni stress, the absorption of nutrients, root development, and metabolism are strongly retarded. Before the acute Ni toxicity

symptoms are evident, elevated concentrations of this metal in plant tissues are known to inhibit photosynthesis and transpiration (Bazzaz et al., 1974). Also low N_2 fixation by soybean plants was reported to be caused by Ni excesses (Vesper and Weidensaul, 1978).

Under natural conditions Ni toxicities are associated with serpentine or other Ni-rich soils. Anderson et al. (1973) reported that oats, a Ni-sensitive crop, when affected by this metal contained Ni in leaves ranging from 24 to 308 ppm (dry wt. basis). The phytotoxic Ni concentrations ranged widely among plant species and cultivars and have been reported for various plants to be from 40 to 246 ppm (dry wt. basis) (Gough et al., 1979). Davis et al. (1978) found the toxic Ni content of barley seedlings to be as low as 26 ppm (dry wt. basis), and Khalid and Tinsley (1980) found 50 ppm (dry wt. basis) Ni in ryegrass to cause slight chlorosis.

Toxicity of Nickel in Plants

In general, when Ni concentrations in vegetative tissues of plants exceed 50 ppm (dry wt. basis), plants may suffer from excess Ni and exhibit toxicity symptoms.

A wide range of levels of Ni in the growth media and in plant tissues has been reported toxic to plants. Mishra and Kar (1974) reported that in nutrient solution, Ni may be toxic to plants at levels as low as <1 ppm to levels as high as 300 ppm (dry wt. basis), depending on the plant species.

With trees, levels $\geq$ 10 ppm Ni in the nutrient solution substantially reduced the growth of white pine and white spruce seedlings (Lozano and Morrison, 1982). In soil, Ni levels can be much higher before phytotoxicity occurs. For example, Khalid and Tinsley (1980) noted no yield depressions and the absence of chlorotic symptoms in ryegrass until at about the 90 ppm (dry wt. basis) level in a non-calcareous (pH 4.7) soil.

In plants, the following toxic levels (ppm dry wt) in the foliage were found: rice, 20-50 (Chino, 1981); ryegrass, 154 (Khalid and Tinsley, 1980); barley, 26 (Davis et al., 1978); hardwood species, 100-150 (Lozano and Morrison, 1981); and citrus, 55-140 (Vanselow, 1951). These results indicate that plants are divergent in their sensitivity to Ni.

Factors Affecting the Availability of Nickel

1. pH

The solubility and plant availability of most heavy metals in soils are known to be inversely related to pH. The effects of pH on Ni chemistry in soils have been demonstrated in soil retention studies, sewage sludge application on land, reclamation of serpentine soils,

plant uptake studies, and others. In soil sorption studies, the amount of Ni retained was dependent upon the pH of the soil, with retention increasing with increasing pH (Harter, 1983; Gerritse et al., 1982). Harter (1983) found that Ni extracted with 0.01 N HCl averaged about 70% to 80% of the amount retained by soils from pH <5.0 to >8.0. However, the percent extractability decreased to <75% of the Ni retained at pH 7 or above. Also pH influences the precipitation of Ni with other compounds, such as phosphates. Pratt et al. (1964) reported that formation of Ni-P complexes could occur at pH values >7.0 thereby reducing Ni toxicity in soils.

In lands receiving sewage sludge high in metal contents, Ni and other metals should not cause toxicity to crops or pose a hazard to the food chain when soils have pH values or 6.5 or greater (CAST, 1976). Liming sludged soils is important since sludge high in ammoniacal-N would tend to acidify the soil through the production of H^+ ions from the mineralization and nitrification of sludge N. John and Van Laerhoven (1976) found that differences in plant tissue Ni concentrations were associated with sludge-lime interaction.

Elevating the pH in soils reduces the amount of exchangeable Ni and, therefore, Ni toxicity to plants. The drastic effect of elevated soil pH on Ni uptake by plants growing on serpentine soils is demonstrated in Figure 23, and by other investigators (Painter et al., 1953;
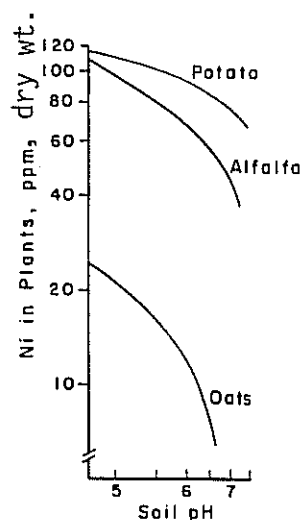

Fig 23. Relationships between soil pH and nickel content (ppm) in selected crops. *Source:* Mizuno. 1968. Reprinted by permission.

Halstead et al., 1969; Bingham et al., 1976; Wallace et al., 1977a).
Bingham et al. (1976) indicated that the critical soil concentration of
Ni was much lower for acid than for calcareous soil. For example, in
wheat as plant indicator, the initial Ni level in soil that produced 50%
yield decrement was 195 ppm in acid soil compared with 510 ppm in
calcareous soil; with Romaine lettuce, the values were 110 and 440 ppm,
respectively, for acid and calcareous soils. Painter et al. (1953)
found that approximately 20% more Ni was removed by alfalfa from plots
having pH lower than 6.8 than from plots having higher pH values.
However, there might be instances where liming the soil at even close to
pH 8.0 may not alleviate Ni toxicity to plants (Soane and Saunder,
1959). Gupta et al. (1987) reported that in case of neutral to alkaline
soils, the average percent Ni uptake of the applicated soil Ni through
lettuce plants was lower than in acid sandy soils.

2.   Organic Matter

Organic matter, depending on its nature, can either immobilize or
mobilize metals. Organic matter has been shown to fix Ni, thereby
rendering it less available to plants (Halstead, 1968; Halstead et al.,
1969).

Guideline

There appears to be no need or justification for changing the
recommended maximum concentration of Ni in irrigation waters spe-
cifically for the west side of the San Joaquin Valley. Consequently, the
previous guideline of 0.2 mg/L (National Academy of Sciences, 1973) is
hereby recommended for continuous use on all irrigated soils including
those on the West Side of the San Joaquin Valley.

We recognize that the pH is the major factor controlling Ni availa-
bility. Thus in alkaline soils the guideline could be increased.
However, the data of Deverel et al. (1984) indicate that there is no
need to increase the present guideline.

LEAD

Lead occurs mainly as Pb^{2+}, although its oxidation state, +4, is also known, and it forms several minerals that are quite insoluble in natural waters. The natural Pb content of soil is inherited from parent rock. However, due to widespread Pb pollution, most soils are likely to be enriched in this metal, especially in the surface horizon. Major anthropogenic sources of Pb that can enrich agricultural soils are auto emissions, industrial deposition, and sewage sludge.

The natural Pb content of soils is strongly related to the composition of the parent material, and Pb is reported to be the least mobile among the heavy metals. The relatively low Pb concentrations in natural soil solutions support this statement (Bradford et al., 1971; Heinrichs and Mayer, 1980). Although the Pb species can vary considerably from one soil type to another, it may be concluded from the results given by Norrish (1975), Riffaldi et al. (1976), Tidball (1976) and Schnitzer and Kerndorff (1980) that Pb is associated mainly with clay minerals, Mn oxides, Fe and Al hydroxides, and organic matter. However, in some soil Pb may be highly concentrated in Ca carbonate particles or in phosphates.

The solubility of Pb can be greatly decreased by liming acid soils. A high soil pH may precipitate Pb as hydroxide, phosphate, or carbonate, as well as promote the formation of Pb-organic complexes.

Hildebrand and Blume (1974), Kabata-Pendias (1980), and Farrah and Pickering (1977) discussed several possible mechanisms of adsorption of hydroxy species and suggested that Pb sorption on montmorillonite can be interpreted as simply cation exchange processes, while on kaolinite and illite Pb is rather competitively adsorbed. Abd-Elfattah and Wada (1981) found a higher selective adsorption of Pb by Fe oxides, halloysite, and imogolite than by humus, kaolinite, and montmorillonite. In other studies, the greatest affinity to sorb Pb were reported for Mn oxides (Kabata-Pendias, 1980; McKenzie, 1980).

The characteristic localization of Pb near the soil surface in most soil profiles is primarily related to the surficial accumulation of organic matter. The greatest Pb concentrations are also often found in the organically rich top horizons of uncultivated soils, as was reported by Fleming et al. (1968). Therefore, organic matter should be considered as the important sink of Pb in polluted soils.

The accumulation of Pb in surface soils is of great ecological significance because this metal is known to greatly affect the biological activity of soils. This topic has been reviewed by Tyler (1975, 1976), Andersson (1976b), Doelman and Haanstra (1979), and Hughes et al. (1980), who showed that increased levels of Pb in soil are likely to limit enzymatic activity of microbiota and as a consequence, markedly

increase the accumulation of incompletely decomposed soil organic matter, particularly those materials that do not decompose readily, such as cellulose. A significant accumulation of nitrates in soils enriched in Pb was observed by Woytowicz (1980).

Niyazova and Letunova (1981) reported a strong tendency of soil microflora to accumulate Pb at a very high rate that was proportional to the metal content of soils. Consumers such as earthworms also at times concentrate Pb from the soil substrata, which greatly contributes to a secondary deposition of Pb in surface soils.

Recently Pb concentrations have gradually increased in soils and may seriously inhibit microbial processes. These effects should be expected principally in soils with a low CEC value. However, in the long run, they may also occur in other soils with a higher CEC.

Sposito et al. (1982) reported that the most dominant fraction of Pb in arid-zone field soils is the "carbonate" regardless of the sludge application rate. The low percentage of Pb in the "exchangeable" and "sorbed" forms could signify a low availability of this metal to plants, since the readily soluble form is often regarded as the most bioavailable. Chang et al. (1984) observed that the forms of Pb in soils were not substantially affected by applications of municipal sewage sludge.

Jurinak and Santillan-Medrano (1974) showed that the basic soils of the arid and semi-arid regions are excellent sink for Pb. The movement of Pb in the percolating water is essentially nil, even in the presence of large amounts of excess salts. The solubility of Pb in soil is about 100 times less than that of Cd, for example, in the pH range of 5 to 9. The Pb-hydroxy species indicate that $Pb(OH)_2$ formation is important above pH 9, while $PbOH^+$ is predominant between pH 6 and 9 (Hahne and Kroontje, 1973). They also indicate by computer simulations for non-soil systems that, in arid and semi-arid areas, soils are not only basic and saline in nature, but high chloride content is often associated with high salinity. Furthermore, chloride is ubiquitous in the natural soil environment and can be regarded as a very mobile and persistent complexing agent for the heavy metals. The chloride ion concentration determines the degree of complexation.

Plants

Lead occurs naturally in all plants, yet is has not been shown to play any essential roles in their metabolism. Broyer et al. (1972) reviewed this topic and concluded that if Pb is necessary for plants, the concentration of 2 to 6 ppb (dry wt. basis) should be sufficient. Lead has recently received much attention as a major chemical pollutant of the environment and as an element toxic to plants.

Zimdahl (1975) and Hughes et al. (1980) extensively reviewed the findings on Pb absorption by roots and concluded that the mode of its uptake is passive and that the rate of uptake is reduced by liming and

by low temperature. Lead, although not readily soluble in soil, is absorbed mainly by root hairs and is stored to a considerable degree in cell walls.

The Pb content of plants grown on mineralized areas is, in general, highly correlated with the Pb concentration in soil, although this relationship differs among organs of the plant (Kovalevskiy, 1979).

When Pb is present in soluble forms in nutrient solutions, plant roots are able to take up great amounts of this metal, the rate increasing with increasing concentration in the solutions and with time (Kovalevskiy, 1979). The translocation of Pb from roots to tops is greatly limited, and as Zimdahl (1975) described, only 3% of the Pb in the root is translocated to the shoot.

The degree to which soil Pb is available to plants is of great environmental concern. Cannon (1976) and Zimdahl and Koeppe (1977) reviewed this topic and showed that in spite of several statements in the literature on the slight effect of soil Pb on concentrations of Pb in plant tissues, plants are able to take up Pb from soils to a limited extent. Apparently most of the Pb in soil is unavailable to plant roots. Wilson and Cline (1966) showed that only 0.003 to 0.005% of the total Pb in soils may be taken up by plants. This uptake, however, varies significantly over the concentration ranges currently present in soils and with the various forms of Pb that occur in soils. The immobile nature of Pb in plant roots is illustrated in Table 15 where very little translocation occurred from roots to the vegetative parts of the crops.

Zimdahl and Koeppe (1977) cited an alternate hypothesis to explain the Pb uptake from soil, in which Pb is not taken up directly from soil by plant roots, but rather is sorbed from dead plant materials accumulated near the soil surface. Nevertheless, there is much evidence that Pb is taken up from soils by roots, at both low and high Pb concentrations, and that this process is strongly governed by soil and plant factors (Merry and Tiller, 1978).

Airborne Pb, a major source of Pb pollution, is also readily taken up by plants through foliage. Much controversy exists in the literature on the question of how much airborne Pb is fixed to hairy or waxy cuticles of leaves and how much Pb is actually taken into foliar cells. A number of studies have shown that Pb deposited on the leaf surface is absorbed by these cells. Although it has been suggested that most of the Pb pollution can be removed from the leaf surfaces by washing with detergents (Albasel and Cottenie, 1984), there is likely to be a significant translocation of Pb into plant tissues (Isermann, 1977).

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Table 15. Translocation of Pb from roots, as indicated by concentrations (in ppm dry wt. basis) in various plant parts, in selected crop species[a].

Crop	Plant part	Control	200 ppm Pb in soil	1,000 ppm Pb in soil
Leaf lettuce	Leaf	2.5	3.0	54.2
	Root	5.8	84.5	867.7
Spinach	Leaf	0.7	7.9	39.2
	Root	4.7	73.3	--
Broccoli	Leaf	7.2	8.4	18.4
	Root	6.5	83.0	745.6
Cauliflower	Leaf	5.3	6.3	11.8
	Root	2.5	55.1	532.2
Oats	Grain	3.2	4.4	4.9
	Husk	11.1	11.8	16.4
	Leaf	6.0	6.8	20.1
	Stalk	1.6	2.5	9.2
	Root	4.5	82.0	396.6
Radish	Tops	3.7	9.9	14.3
	Tuber	6.3	7.0	44.6
Carrot	Tops	2.3	8.0	17.6
	Tuber	1.9	5.3	41.0
	Root	8.9	241.7	561.4

[a]Source: John and Van Laerhoven, 1972, with permission of the Department of Agriculture. Government of Canada.

cells. A number of studies have shown that Pb deposited on the leaf surface is absorbed by these cells. Although it has been suggested that most of the Pb pollution can be removed from the leaf surfaces by washing with detergents (Albasel and Cottenie, 1984), there is likely to be a significant translocation of Pb into plant tissues (Isermann, 1977).

Sewage sludge, especially those from metropolitan areas, added in large quantities to land can enrich the soil environment and possibly also increase the Pb contents of plants (Sommers et al., 1976; Page, 1974). Page (1974) indicated that enrichment of plant tissues by sludge-borne Pb was unlikely. More recent studies indicate that, while the soil might be enriched by sludge-borne Pb, its uptake by crops should seldom be of major concern as far as the food chain is concerned (Kirkham, 1975; Dowdy and Larson, 1975; Zwarich and Mills, 1979; Soon et al., 1980).

The North Central Regional Technical Commitee, in cooperation with the Western Regional Technical Commitee, published suggested limits for the total amount of sludge metals allowed on agricultural lands

(Adriano, 1986). The guidelines are based upon the cation exchange capacity CEC (meq/100 g) of soils having pH of 6.5 or more. For soils with CEC values of <5, 5-15 and >15, respectively, the limits were 560, 1,120, and 2,240 kg Pb/ha.

It has been concluded that since Pb added to soils is usually not readily available to crops, accumulation of this element in crops would not limit the application of sludge to land (CAST, 1976).

Because Pb enters the soil in various and complex compounds, its reactions may differ widely among areas. Indeed, opinion appears to differ as to whether Pb as a pollutant is a mobile or a stable soil component. Tyler (1981) reported that Pb is the most stable metal in forest soil, and the time necessary for a 10% decrease of its total concentration by leaching was calculated to be 200 years for polluted soil and 90 years for "control" soil. Kitagishi and Yamane (1981) calculated the period in which the amount of Pb in soil will decrease by one half to range from 740 to 5900 years, depending on the kind of soil, the water management, and the organic matter present. Stevenson and Welch (1979) observed that Pb moved from the top soil treated with Pb acetate into the subsoil, even though the soil (silty clay loam) was shown to have a high capacity for binding Pb in nonexchangeable forms. This mobility was attributed to the metal leaching as soluble chelated complexes with organic matter. It must be emphasized that contamination of soils with Pb is mainly an irreversible and, therefore, a cumulative process in subsurface soils will continue, even if inputs are low.

Guideline

The previous recommendation that the Pb concentrations in irrigation waters not exceed 5 mg/L (National Academy of Sciences, 1973) appears to be adequate for the west side of the SJV. Larger concentrations might be tolerated for the fine-textured alkaline soils of the west side. On the other hand, there is no reason to suspect that any irrigation waters in the SJV will exceed the 5 mg/L value. Deverel et al. (1984) reported maximum concentrations of Pb did not exceed 0.05 mg/L.

Lead in soils is highly stable and very insoluble and unavailable to plants. But, because of its insolubility added Pb has extremely low mobility which means that it accumulates in surface soils. Centuries are required for removal of any substantial fraction of the Pb in polluted soils. Absorption and translocation of Pb in plants is also extremely low and does not represent a hazard. However, Pb deposited on leaves through sprinkler systems from irrigations waters containing elevated concentrations of Pb and Pb attached to root crops grown in soils with elevated Pb concentrations could present hazards. Thus, the Pb concentrations in irrigation waters should be kept as low as possible.

VANADIUM

The geochemical characteristics of V are strongly dependent on its oxidation state (+2, +3, +4, and +5) and on the acidity of the media. This metal is concentrated mainly in mafic rocks and in shales, ranging from 100 to 250 ppm. Vanadium is known to form various complexes of cationic and anionic oxides and hydroxy oxides (Garrels and Christ, 1965). Therefore, V displays various behaviors.

In general, the behavior of V in soil has received little attention. Norrish (1975) reported that Fe oxides hold a reasonable fraction of the soil V that is more mobile and could supply V to plants.

Apparently, the vanadyl cation (VO^{2+}) may be an important form of V in many soils and may result from reduction of the metavanate anion (VO_3^-). Goodman and Cheshire (1975) and Bloomfield (1981) stated that much of the soil V, mainly the vanadyl cation is mobilized as complexes with humic acids. Also anionic forms (that predominate in neutral and alkaline conditions) of V (VO_4^{3-}, VO_3^-) are known to be mobile in soils and to be relatively more toxic to soil microbiota.

Vanadium is not considered to be an essential element for higher plants. Welch and Huffman (1973) did not obtain any growth response of lettuce and tomato plants to added V. However, some evidence exists to suggest that it is essential for the growth of certain bacteria and algae (Arnon and Wessel, 1953; Hopkins and Mohr, 1971). Dobritskaya (1969) reported a high accumulation of V in nodules of several legumes (3 to 12 ppm dry wt. basis), which suggests the V association with N_2 biofixation. However, no evidence of V deficiency in higher plants was observed, and Welch and Cary (1975) claimed that if V is essential for plants, adequate levels in their tissues are less than 2 ppb dry weight. The evidence, therefore, that V is essential for the growth of higher plants is not yet conclusive (Epstein, 1965; Gauch, 1972; Pratt, 1966).

Welch (1973) reported that V is passively absorbed by barley roots. The uptake was a linear function of V concentration and was highly dependent on pH. These results indicate that VO^{2+} species occurring under acid conditions are more rapidly absorbed by roots than are VO_3^- and HVO_4^{2-} species that predominate in neutral and alkaline solutions. However, both cationic and anionic species are capable of being chelated and thus could contribute substantially to V uptake by plants from soils, but no significant relationship between vegetation and soil V has been reported (Parker et al., 1978).

The reported variation in V content of plants may be an effect of both analytical difficulties and pollution. Values given by Shacklette et al. (1978) in some food plants as ppb, dry wt. basis, were: lettuce 1080, apple 330; potato 1490; carrot 990; beet 880; and pea 460. These values apparently reflect a pollution source of V.

Gough et al. (1979) stated that there are no reports indicating V toxicity under field conditions. However, under man-induced conditions, V as high as 0.5 ppm in the nutrient solution, and 140 ppm in the soil solution, may be toxic to plants. Phytotoxicity of V may appear at about 2 ppm, dry wt. basis, V in plant tissues (Davis et al., 1978). Wallace et al. (1977b) reported that bush beans absorbed from culture solutions as much as 13, 8, and 880 ppm V in leaf, stem and root (dry wt. basis), respectively, and that this resulted in smaller growth but not chlorosis.

Guideline

The toxicity of V manifested in nutrient solutions and in soils were used as justification for the prior recommendation that V in irrigations not exceed 0.1 mg/L (National Academy of Sciences, 1973). Thus, reported research provides no basis for modifying the recommendation for the west side of the SJV or any other area. The range of V reported by Deverel et al. (1984) was between <1 and 280 ug/L (with median value of 14 ug/L).

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